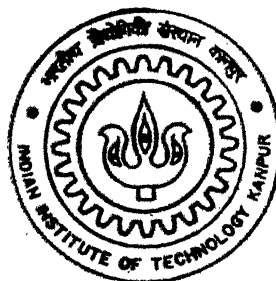


ELECTROREMEDIATION OF SOIL CONTAMINATED WITH Cr(VI): POTENTIOSTATIC VS GALVANOSTATIC MODE OF OPERATION

By

Preeti Prakash sahuo



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DEPARTMENT OF MATERIALS AND METALLURGICAL ENGINEERING

Indian Institute of Technology Kanpur

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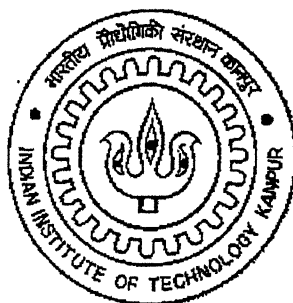
ELECTROREMEDIATION OF SOIL CONTAMINATED WITH Cr(VI): POTENTIOSTATIC VS GALVANOSTATIC MODE OF OPERATION

A Thesis submitted
in Partial Fulfillment of the Requirements
for the degree of

MASTER OF TECHNOLOGY

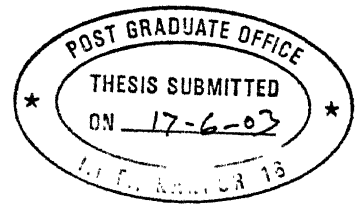
By

Preeti Prakash sahuo



**DEPARTMENT OF MATERIALS AND METALLURGICAL
ENGINEERING**

INDIAN INSTITUTE OF TECHNOLOGY KANPUR
June 2003



CERTIFICATE

This is to certify that the investigation on "**Electroremediation of soil contaminated with Cr(VI): Potentiostatic Vs Galvanostatic mode of operation**" has been carried out by Mr PREETI PRAKASH SAHOO (Roll No – Y110612) dissertation under my guidance and it has not been submitted elsewhere for a degree.

A handwritten signature in black ink, appearing to read "R. Shekhar".

(Dr. R Shekhar)

Professor

Department of Materials and Metallurgical Engineering
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Dated: June, 2003

Dedicated to

My parents.

ACKNOWLEDGEMENTS

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Preeti prakash Sahoo

Date: 26th June

ABSTRACT

Electroremediation is emerging as a viable, cost effective technique for cleaning heavy metal contaminated soils. The major objective of this investigation is to select the mode of power source to be used for different kind of soil for the energy efficient removal of Cr(VI). Therefore experiments have been carried out under potentiostatic and galvanostatic mode of operation on synthetic kaolin and Kanpur soil spiked with synthetic $K_2Cr_2O_7$. A maximum of 47% chromium was removed from kaolin for Cr(VI) contaminated soil under potentiostatic mode but in case of galvanostatic mode the removal is much higher around 90 percentages. Migration of the acid and base fronts leading to acid-base neutralization adjacent to the cathodic end of kaolin appears be the rate-controlling step. Removal of chromium from Kanpur soil was more efficient than in kaolin in potentiostatic mode approximately 75-85% chromium being removed in the first 40 hours but with the galvanostatic mode only 65% can be removed after 72 hours. The difference in the remediation efficiency in kaolin and Kanpur soil can be attributed to the nature of the soil; the former is weakly acidic ($pH = 5.5$), while the latter is basic ($pH = 10$). Moreover, Kanpur soil is strong basic buffer. In case of Kanpur soil constant voltage condition is favorable but in case of kaolin constant current condition is favored, considering the energy efficiency and removal percentage. It can also be concluded that the best operating condition is to operate with galvanostatic mode for first 30 hours and after that potentiostatic mode, for higher percentage removal in case of kaolin or low pH soil.

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CHAPTER 1

INTRODUCTION

1.1 Introduction to Soil Cleaning:

Every year millions of tonnes of hazardous waste are generated in the world. Due to inefficient waste handling techniques and hazardous waste leakage, thousands of sites are contaminated by heavy metals, organic compounds and other hazardous materials, which made an enormous impact on the quality of ground water, soil and associated ecosystems. Toxic heavy metals in solid wastes are leached by rainwater, which contaminates the soil as it migrates through the subsurface. The contamination by these heavy metal not only affects the ground water as well it very much liable to contaminate the crops grown on the site [1]. Earlier the soil was excavated from the contaminated site and then refilled after cleaning it. But this process is not cost effective and need lot of engineering equipments. Now days more emphasis is given on the insitu remediation technique for the soil treatment. There are different techniques for insitu remediation of contaminated soil. But the most promising process for decontamination of soil is electrokinetic remediation process, which is capable of removing heavy metals as well as organic contaminants from soil, safely.

1.2 Methods of cleaning contaminated Soil:

- 1) The other methods for the insitu soil cleaning are:
- 2) Phytoremediation
- 3) Percolation leaching
- 4) Bioremediation
- 5) Insitu vitrification (ISV)
- 6) Electrokinetic soil remediation

In **phytoremediation** technique small plants are grown on the soil surface. These plants are capable of absorbing toxic heavy metals. Once the plants are grown then these are

then uprooted and burned somewhere away. But this process has certain disadvantages, such as this process take longer time for the plants to grow and also it can clean the soil up to certain centimeter depth.

Percolation leaching technique [2,3] is extensively practiced for the heap leaching of lean nonferrous ore such as copper and silver. Large pores of soil are flushed away by this process removing the contaminants but the small pores remain untouched. The adsorption of heavy metal ions takes place in the smallest pores due to stronger electrostatic forces in it. That's why this technique is applicable for large permeability soils.

In **bioremediation** [4], micro orgasms capable of transferring heavy metals, organic compounds are applied on the subsurface of the soil by special bioelectric technology, which consumes the contaminants. But this process is not so much reliable as sometime the concentration of the contaminants exceeds the toxic limit at which the micro orgasms get destroyed or they produce harmful byproducts.

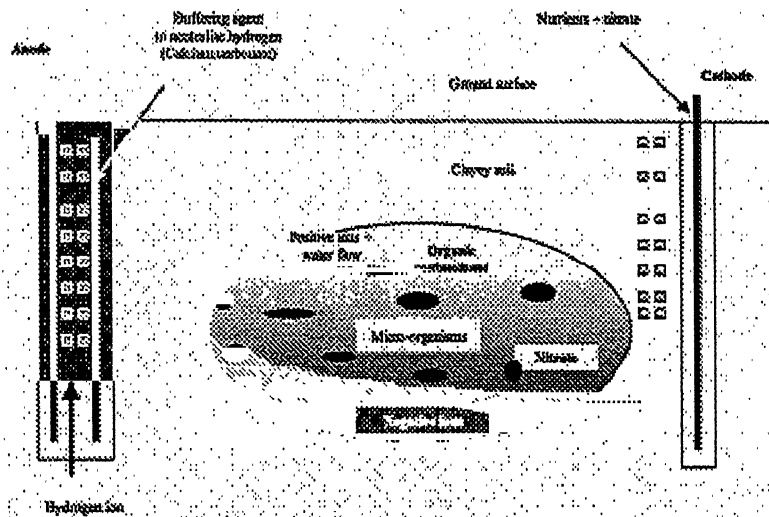


Fig: 1.1 Electrokinetic Bioremediation (according to Thevanayagam and Rishindran)

Insitu vitrification (ISV) is a process, which uses electrical power to heat and melt soil contaminated with organic, inorganic, and metal-bearing wastes. The molten material cools to form a hard, monolithic, chemically inert, stable glass and crystalline product that incorporates the inorganic compounds and heavy metals in the hazardous waste. The organic contaminants within the waste are vaporized or pyrolyzed and migrate to the surface of the vitrified zone where they are oxidized under a collection hood. Residual emissions are captured in an off-gas treatment system.

Chromium exists in three forms such as Cr, Cr(III) and Cr(VI). Among these Cr(VI) is toxic and carcinogenic in nature. It is released from a variety of sources such as tanneries, distilleries, and electroplating units and also from other chemical industries. Considering for the protection of public health and the environment, attention has been focused on the development of a cost effective, insitu technology for treating Cr(VI) contaminated soil.

A relatively new and potentially important technique has immersed in which DC electric field is applied across two electrodes placed the ground. The contaminants in ionic form in the soil move under the action of electric field to the wells and then pumped out. The principal mechanisms under which the ions travel are electroosmosis and electromigration. Electroosmosis is effective in fine-grained soil where the pores are small, but electromigration is independent of the pore size. Another advantage of this technique is the high degree of control of flow direction that can be achieved because the materials move along electric field lines that are defined by the electrode placement. A number of laboratory experiments and very few field experiments have demonstrated the viability of the process of cleaning heavy metal from soils. These studies have highlighted the phenomena that affect the cleaning efficiency such as nature of soil, evolution of pH profile, precipitation and adsorption of heavy metals. But very little attention has been given on Cr(VI) contamination and non of these studies have focused on the kinetics, unremediated chromium, associated rate controlling mechanism, and nature of power to be supplied for different kind of soil.

The objective of this work is to show the efficacy of the electrochemical cleaning process and to estimate the nature of power to be supplied for different kind of soil.

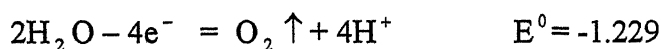
1.3 Principles of electrokinetic remediation

Electrokinetic soil remediation technology uses a low level direct current, in the orders of milliamps per cm^2 of soil cross-sectional area, to transport and recover ionic species from soils. Upon application of this current the soil-water-electrolyte system undergoes physicochemical and hydrological changes leading to contaminants transport and removal. The applied electric current (or electric potential difference) leads to electrolysis reactions at the electrodes, acid-base distribution drive by chemical, electrical, and hydraulic potential differences, adsorption/desorption, transport of the pore fluid and ions.

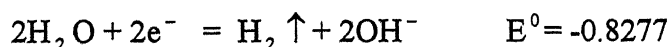
1.4 Electrolysis reactions

When electric potential is applied through electrodes immersed in water induces electrolysis reactions in the immediate vicinity of Electrodes. Oxidation of water at the anode generates an acid front while reduction at the cathode produces a base front. The electrolysis reaction at the electrodes are presented by the following equations:

Anode reaction:



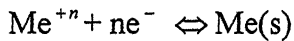
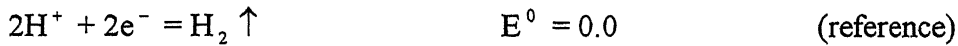
Cathode reaction:



Where E^0 is the standard reduction electrochemical potential, which is a measure of the tendency of the reactants in their standard states to proceed to products in their standard states. The acid medium (H^+ ions) generated at the anode advances through the soil toward the cathode by ion migration due to electrical gradient, pore-fluid flow due to any

externally applied or internally generated hydraulic gradient and diffusion due to the chemical gradients developed in the system.

Secondary reactions may exist depending upon the concentration of available species, e.g.,



Me refer to metals. The prevailing of electrolysis reactions at the electrode depends on the availability of chemical species and the electrochemical potentials of these reactions. Although some secondary reactions might be favored at the cathode because of their lower electrochemical potential, the water reduction half reaction ($2\text{H}_2\text{O} / \text{H}_2$) dominates at the early stages of the process. At the latter stages, the acid front advances towards the cathode carrying H^+ and other cations. Within the first 100 hours of processing, electrolysis reactions will drop the pH at the anode to below 2 and increase it at the cathode to above 12, depending upon the total current applied [6-7].

1.4.1 Effect of electrolysis reaction

Due to the electrolysis reaction at the electrodes acid front is generated at the anode, which advance towards the cathode. This transport is governed by ionic migration

1.5 Different transport processes for ions in soil

Application of electric, hydraulic, thermal or chemical gradient in soil-water-electrolyte system result in transport of matter as well as energy. Thus resulting fluxes of fluid, charge, mass, and heat through the soil medium. The changes that occur to this flux with

time and their effects on the properties and composition of the soil are significant in geo-environmental problems.

The fluxes through the soil medium can be categorized as two types; uncoupled fluxes and coupled fluxes. Direct or uncoupled fluxes result due to application of potential gradient, concentration gradient, temperature gradient etc (conjugate driving forces).. Examples of direct fluxes are heat flux due to temperature gradient (Fourior's Law), mass flux due to concentration gradient (Fick's Law), fluid flux due to hydraulic gradient (Darcy's Law) and charge transport due to electric gradient (Ohm's Law). Coupled fluxes results due to non-conjugate driving forces. One example of such flux is mass transport due to thermal gradient by convection.

In soil-water-electrolyte system the coupled fluxes are water transport due to electric gradient (electroosmosis), heat transport due to chemical gradient (Dufore effect), and charge transport due to thermal gradient (Soret effect).

So the transport of matter in soil-water-electrolyte system is primarily due to:

1. Electroosmosis
2. Electromigration
3. Hydraulic gradient (Darcy's Law of Advection)
4. Diffusion

1.5.1 Electroosmosis (Fig 1.2)

The Helmholtz-Smoluchowski theory for the electroosmosis is the most commonly adopted theoretical description of fluid transport through soils due to electrical gradients. Similar to the hydraulic conductivity, this theory introduces the coefficient of electroosmotic permeability, k_e , as the volume rate of fluid flowing through a unit cross sectional area due to a unit electrical gradient.

$$J_w^e = k_e \nabla(-E) = k_e I$$

Where k_i is the electroosmotic coefficient of fluid transport given by,

$$k_i = \frac{k_e}{\sigma^e} \quad \text{Where } \sigma^e \text{ is the effective electrical conductivity of the soil}$$

medium.

The value of k_e is widely accepted to be a function of zeta potential, viscosity of the pore fluid, porosity and electrical permittivity of the soil medium. When the soil pores are treated as the capillary tube, the coefficient of electroosmotic permeability is given by,

$$k_e = \frac{\varepsilon \varepsilon_0 \zeta}{\eta} n \quad \text{Where } \varepsilon \text{ is the permeability of the medium, } \zeta \text{ is the zeta}$$

potential, n is the porosity, and η is the viscosity.

Electroosmotic flow rate depends on the balance between the electrical force on the liquid and the friction between the liquid and the surface of the soil particles [5]. For a simple model of soil made up of parallel cylindrical capillaries the electroosmotic velocity is given by

$$u_e = -\varepsilon \zeta E / \eta$$

Mitchell [8] in an extensive summary of theoretical and experimental treatise of the zeta potential in colloid science displays the effect of pH and ion concentration in the pore fluid on zeta potential. The effect of electrolyte chemistry on zeta potential could therefore represented by Kruit [9],

$$\zeta = A - B \log C_0$$

Where, A and B are two constants that are evaluated experimentally, and C_0 is the total electrolyte concentration.

Electroosmosis: Water Transport from anode to cathode
 Electromigration: Ion Transport to the opposite electrode

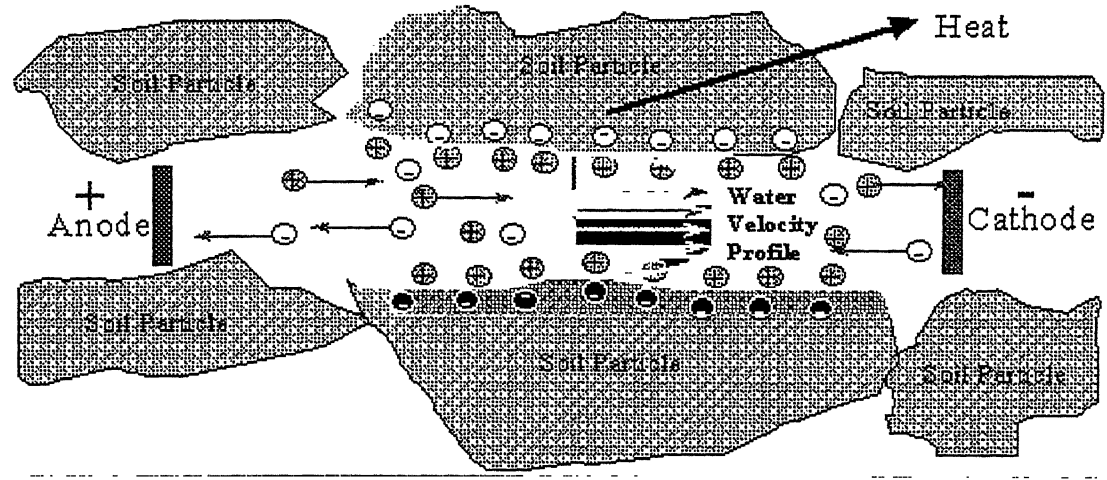


Fig 1.2: Electroosmosis and Electromigration of ions in soil (Terran Corporation)

1.5.2 Electromigration (Fig 1.2)

The migrational mass flux of the free ionic species in the soil pore fluid due to the applied electric field is given by,

$$J_i^e = u_i^0 c_i \nabla(-E)$$

Where J_i^0 is the migrational mass flux of the i^{th} species, and u_i^0 is the effective ionic mobility of the i^{th} species. The effective ionic mobility, u_i^0 , defines the velocity of the ion in the soil pores under unit electric field

$$u_i^0 = n \tau u_i = \frac{D_i^0 z_i F}{RT}$$

Where u_i is the ionic mobility of species I at infinite dilution, z_i is the charge of the i^{th} species, D_i^0 is the molecular diffusion coefficient, F is the Faraday's constant, R is the

universal constant, τ is the tortuosity of the soil medium, n is the porosity of the medium and T is the absolute temperature.

1.5.3 Hydraulic gradient (Darcy's Law of Advection)

Fluid flow due to a hydraulic gradient, $J_w^h(LT^{-1})$ is given by Darcy's law as,

$$J_w^h = k_h \nabla(-h)$$

where k_h is the coefficient of hydraulic conductivity, h is the hydraulic head ($h = u/\gamma_w$), u is the hydraulic potential, and γ_w is the unit weight of the pore fluid.

1.5.4 Diffusion (Fick's Law)

The diffusive mass transport of chemical species in a saturated soil medium, under chemical concentration gradients is described by Fick's first law,

$$J_i^d = D_i^0 \nabla(-c_i)$$

where J_i^d is the diffusive mass flux of the i^{th} chemical species per unit cross sectional area of the porous medium, c_i is the molar concentration of the i^{th} chemical species, D_i^0 is the effective diffusion coefficient of the i^{th} chemical species.

1.6 Major Factors Affecting Electroremediation

1.6.1 Electrolyte Composition and pH

With time the removal of metal ions takes place. So the concentration of certain metal ions decreases with time and the composition of the pore fluid changes.

The predominant process in moist soil is the electrolysis of water, which results in the formation of H^+ ion and oxygen at anode and OH^- ions and hydrogen at cathode. The immediate change in soil is the pH of the pore fluid due to migration. Acidity increases at the anode and alkalinity increases at the cathode.

An acid front moves across the soil sample from the anode towards cathode and a base front moves from the cathode to anode. The acid front moves faster than the base front because the mobility of H^+ ion is greater than the OH^- ion, and the direction of electroosmotic flow is from anode to cathode. So after sometime the whole soil mass except some distance from the cathode becomes acidic and the part nearer to cathode stay basic. But if the soil has a high buffering capacity then this phenomenon may not be observed. Where the acid and base fronts meet, water is formed resulting in a sharp change in pH, which affects the solubility of the contaminants and there adsorption in the soil [10]. Successful decontamination depends on maintaining metal ion solubility with either a low or high pH throughout the soil and avoiding the conditions resulting precipitation and adsorption.

1.6.2 Electrical Conductivity and Field Strength

As a result of the changes in pH and ionic strength, which arise during electroremediation, nonuniform electrical conductivity and voltage profiles quickly develop. The noticeable drop of conductivity and rapid change in field strength are generally observed near the cathode. This change corresponds to the sharp jump in pH due to neutral layer formation.

The resultant steep potential gradient near the cathode initially causes a higher rate of electroosmotic flow in this region.

1.6.3 Zeta potential

The shear plane (slipping plane) is an imaginary surface separating the thin layer of liquid bound to the solid surface and showing elastic behavior from the rest of liquid showing normal viscous behavior. The electric potential at the shear plane is called zeta potential.

Zeta potential of most of the soil is negative, because soil surfaces carry negative charge. The result is that the electroosmotic flow is generally toward the cathode [5]. However, both pH and ionic strength of the pore fluid, which change continuously during electroremediation affect the value of zeta potential. Increased acidity causes the zeta potential to become less negative and even to attain positive values at low pH. Flow rates have been observed to decrease if the pH of the electrolyte is depressed below neutral, and to increase at alkaline pH values.

There are also other factors, which affect the removal of heavy metal from soil. Some of these are:

- 1 The soil chemistry by which we can know the buffering capacity of soil, which affects the pH variation in the soil section.
- 2 Moisture content in the soil which affects the electroosmotic flow rate and hence decontamination of soil
- 3 Soil structure also affects the removal efficiency.

1.7 Source of Chromium(VI)

The different sources of Cr(VI) which contaminate soil are:

1. Primary metal producing plants
2. Metal processing industries, those involve with electroplating
3. Distilleries
4. Tanneries
5. Thermal power plants
6. Municipal sludge

2.1 Previous Works on Electrokinetic Remediation of Soil

Most of the previous studies on electrokinetic remediation of soils have focused on cationic contaminants. Few studies have been reported on the removal of anionic contaminants by electrokinetic remediation. Only few investigations have been carried out to evaluate the electrokinetic removal efficiency of chromium from contaminated soils.

Lindgren et al.[10] studied the feasibility of using electrokinetics to remove anionic contaminants, similar to chromate ion, from saturated and unsaturated sands. They conducted experiments which consisted of transport visualization of dye in sand, under both saturated and unsaturated conditions, with a constant current of 10mA being applied. Sand obtained from a chemical waste landfill was used in this study. The rate of electromigration of the dye in an imposed electric field was monitored photographically. The characteristics of the electromigration rate were reported to be similar in both tile saturated and unsaturated sand. The electromigration rate was also observed to be concentration dependent. The more diluted dye migrated at a faster rate than the concentrated dye, which resulted in a diffuse leading edge and a sharp, concentrated trailing edge.

In another series of experiments, Lindgren et al. [10] studied the effect of moisture content on the electromigration rate of anionic contaminants and compared the migration behavior of chromate ions with that of surrogate dye ions. Both sodium dichromate and pure FD&C Red No.40 were used as contaminants. The molar concentration of the contaminant, either dye or chromate, in the pore water was kept constant at 0.02 M for all of the experiments. A constant current of 10 mA was applied to the soil for up to 24 h. For the experiments conducted with the dye, photographs of the dye locations were taken at one hour intervals. These experiments revealed that maximum electromigration

occurred at an optimum moisture content of 14 to 18% for the soil tested. The experiment conducted with chromate showed that Cr(VI) migrated towards the anode. A mass balance analysis performed after this test could only account for 56% of the initially introduced chromate. To determine whether the chromate was adsorbed on the graphite electrode, additional special analyses were performed on the electrodes. These analyses showed that a significant amount of Cr(VI) had adsorbed to the anode graphite electrode. This study also reported that part of the Cr(VI) may have been reduced to Cr(III).

Hamed and co-workers [11] investigated the electrokinetic removal of Pb from saturated kaolinite specimens loaded with 118 to 145 μg of Pb(II) per gram of dry soil. 75 to 95% of the adsorbed Pb(II) was removed by this process. The energy requirement was 17 kWh - 35 kWh per ton of soil, or of the order of \$12 per ton of soil, significantly less than the cost of the present techniques that varies between \$30 and \$875 per ton of soil.

Reddy and co-workers [10] conducted electroremediation experiments on three types of soils: glacial till, kaolin and Na-montmorillonite in order to investigate the effect of soil mineralogy on the removal of chromium. Results showed that Cr(VI) removal was most efficient in glacial till, a phenomenon attributed to its buffering capacity that minimised the readsorption of chromium ions. This study has shown that soils which contain high carbonate buffers, such as the glacial till, hinder the development of an acid front, which results in alkaline conditions through out the soil during electro kinetic remediation. However, soil processing low buffer capacity, such as kaolin and Na-montmorillonite, favour the development of an acid front which results in a distinct pH gradient with pH values varying from 2 near the anode to 11 near the cathode.

Generally, discrete clay particles have a negative surface charge that influences and controls the particle environment. This surface electric charge can be developed in different ways, including the presence of broken bonds and due to isomorphous substitution [12]. The net negative charge on the clay particle surfaces requires an excess positive charge (or exchangeable cations) distributed in the fluid zone adjacent to the clay surface forming the diffuse double layer.

Several theories have been proposed for modeling charge distribution adjacent to clay surface. The Gouy-Chapman diffuse double layer theory has been widely accepted and applied to describe the clay behavior.

Electrokinetics is defined as the physicochemical transport of charge, action of charge particles, and effects of applied electric potentials on formation and fluid transport in porous media. The presence of diffuse double layer gives rise to several electrokinetic phenomena in soils, which may result from either the movement of different phases relatives to each other due application of electric field. The electrokinetic phenomena include electroosmosis, electrophoresis, streaming potential, and sedimentation potential. Electroosmosis is defined as fluid movement with respect to a solid wall as a result of an applied electric potential gradient. In other wards, if the soil is placed between the two electrodes in a fluid, the fluid moves from one side to the other when an electromotive force is applied. Electrophoresis is the movement of solids suspended in a liquid due to application of potential gradient. Streaming potential is the reverse of electroosmosis. It defines the generation of an electric potential difference due to fluid flow in soils. Sedimentation (or migration) potential, known as Dorn effect [13], is an electric potential generated by the movement of particles suspended in a liquied.

DC electric fields have been used for a number of applications such as improving stability of excavations; stability of fine-grained soils; dewatering of foams, sludge, and dredging. The principal mechanism involved in these applications was "**electroosmosis**." In an early study Jacobs and Mortland [14] demonstrated that Na^+ and K^+ ions can be leached out of clays by electroosmosis. Krizek and co-workers [15] showed that soluble ions content substantially increased in the effluent after electroosmotic consolidation of polluted dredging. Segal and co-workers [16] discovered that heavy metals concentration in the effluent after electroosmotic consolidation of sludge. The electroosmotic flow rate is directly proportional to the zeta potential. Vane and Zang [17] investigated the effect of pH on clay particle zeta potential on two different soils, Georgia kaolinite and Wyoming bentonite. The zeta potential for the kaolinite ranged from +0.7 mV at pH=2 to -54 mV at pH=10 while the bentonite zeta potential changed by only 5 mV (-31 to -36 mV).

Pamucku and Wittle [18] and Coletta and co-workers [19] also successfully removed heavy metal from soil. Lageman and co-workers [20] report laboratory experiments where heavy metals Cd, Cr, Ni, Pb, Hg, Cu, Zn and As were successfully removed from agrillaceous sand and river mud.

Puppala and co-workers [21] investigated the feasibility of heavy metal removal from high sorption capacity soil by the use of acetic acid to neutralise the cathode electrolysis reaction and also the use of an ion selective membrane (Nafion) to prevent back transport of OH^- generated at the cathode. Acetic acid and Nafion enhancement resulted in better removal efficiencies of lead from a synthetic soil consisting of 40% illite, 8% kaolinite, 5% Na-montmorillonite and 47% fine sand.

Li and Neretnieks [22] countered the problem of metal hydroxide precipitation by placing a tube length of conductive solution, simulating groundwater between the soil and the cathode. However, the length of the conductive solution was relatively large, twice that of the soil being treated. Using this technique, Li and co-workers [23] achieved metal removal efficiencies of 90% with respect to lead (II), cadmium (II) and chromium (III) from sand. Li and co-workers [24] reduced the volume of water needed considerably by placing a cation selective membrane in front of the cathode. Experiments showed that 90% of copper could be removed from sand, and energy consumption was 20 kWh/ton of soil.

Hansen and co-workers [25] investigated the electrodialytic remediation of heavy metal polluted soil, a variant of the conventional electroremediation technique. This method combines electrodialysis with the electromigration of ions in the polluted soil. The cell consists of three compartments; two electrode compartments and a soil compartment placed between them. The catholyte is separated from the soil by a cation exchange membrane and the anolyte is separated from the soil by an anion exchange membrane. When the current is passed through the cell, no current carrying ions can pass from the electrode compartments into the soil due to the ion exchange membranes, while ions can

be transported from the soil into the electrode compartments. In this system current is thus prevented from being wasted in carrying highly mobile ions from one electrode compartment, through the soil, into the other electrode compartment. Hansen and co-workers [26] carried out experiments on soil samples from three contaminated sites, with pollution originating from a wood preservation factory (Cu, Cr), a chlor-alkali plant (Hg), and a copper rolling mill (Cu, Pb, Zn). The electrodialytic remediation process was very effective in removing copper and to a certain extent chromium. However, only 23 % of the Hg could be removed. From the experiments it was also seen that the effect of pH on the desorption of heavy metals from the soil is important. In particular, copper, zinc, and lead seem to desorb at acidic pH values between 3 and 4. Chromium needs a pH of around 2.5 for desorption.

Very few studies on pilot-scale and actual field experiments have been reported. Acar and Alshawabkeh [26] studied the feasibility and efficiency for removing lead at pilot scale in three 1 ton Georgia kaolinite specimens. Subsequent to 2,950 h of processing and an energy expenditure of 700 kWh/m³, 55% of the lead removed across the soil was found precipitated within the last 2 cm close the cathode. 15% of lead was readsorbed in the soil, while 20% was found precipitated on the fabric separating the soil from the cathode compartment. Lageman and co-workers [20] report four field experiments of electroremediation of heavy metal contaminated soil carried out in the Netherlands.

Hamed and Bhadra [29] investigated on the influence of current density and pH on electrokinetics. They conducted experiments with different current density and taking different pH of the influent. The resulted that increasing the current density reduces the time needed for the acid front generated at the anode to reach the cathode. Increasing the pH increase the electroosmotic flow and a sharp increase from 10-12 pH. Increasing current density increased the energy consumption for the same ideal case.

Significant changes in exchangeable and soluble fractions occurred after electrokinetic treatment [27].

Under certain conditions, electroosmosis will have a significant role in electrokinetic soil remediation. Several theories are established to describe and evaluate water flow by electroosmosis. Helmholtz-smoluchowski model is the most common theoretical description of electroosmosis and is based on the assumption of fluid transport in the soil pores due to transport of the excess positive charge in the diffuse double layer towards the cathode.

2.2 Scope/Objective of The Present Investigation

Several studies have been carried out for the electroremediation of heavy metals from contaminated soil. There are very few works on the Cr contamination. The experiments were carried out with different voltage and current conditions. Here the main objective of the investigation is to determine the nature of power source to be used for efficient removal of Cr from contaminated soil with different nature.

Soils may have pH in basic range or in acid range. So for removal of contaminants different types of power source (Constant current/Constant voltage) are to be used for the efficient removal.

CHAPTER 3

EXPERIMENTAL STUDIES

3.1 Operational Details for the Experiments

Table 3.1 shows the operational details of the experiment conducted. From this Table it can be seen that each experiment was carried out for 72 hours because from the studies by Manna [32] it has been observed that in case of Kanpur soil there is almost no Cr removal after first 40 hours. Experiments were also carried out with kaolin for 6 days and the results are same as in soil. There the rate of removal is too low after 70 hours.

Table: 3.1 Operational conditions maintained for the removal of Cr (VI) from soil

Sl. No.	Soil type	Volts or mAs	Initial pH	Experiment duration
1	Kanpur soil	25-volts	10	72 Hrs.
2	Kanpur soil	35-volts	10	72 Hrs.
3	Kanpur soil	5mA	10	72 Hrs.
4	Kanpur soil	10mA	10	72 Hrs.
5	Kaolin	15-volts	5.5	72 Hrs.
6	Kaolin	25-volts	5.5	72 Hrs.
7	Kaolin	35-volts	5.5	72 Hrs.
8	Kaolin	10mA	5.5	72 Hrs.
9	Kaolin	15mA	5.5	72 Hrs.
10	Kaolin	25mA	5.5	72 Hrs.

Constant voltage experiments were carried out under 15, 25 and 35 volts for kaolin.

Constant current experiments were carried out at 10, 15 and 25milli amperes.

First experiments were carried out in potentiostatic conditions. The average current observed in these experiments were then used for the galvanostatic experiments. For 15-volt experiment it can be observed from Fig 4.1 that the average current obtained in 72 hours is 9-10mA. So to compare with 15-volt experiment 10mA was chosen for constant amperage experiment. Similarly for comparing with 25-volts and 35-volts experiments

the current chosen were 15mA and 25mA respectively. Similarly for Kanpur soil experiments were carried out with 25-volts and 35-volts experiment and as can be seen from Fig 3.1 the average current in this experiments are 5mA and 10mA respectively. So the galvanostatic experiments were carried out at these milli amperes.

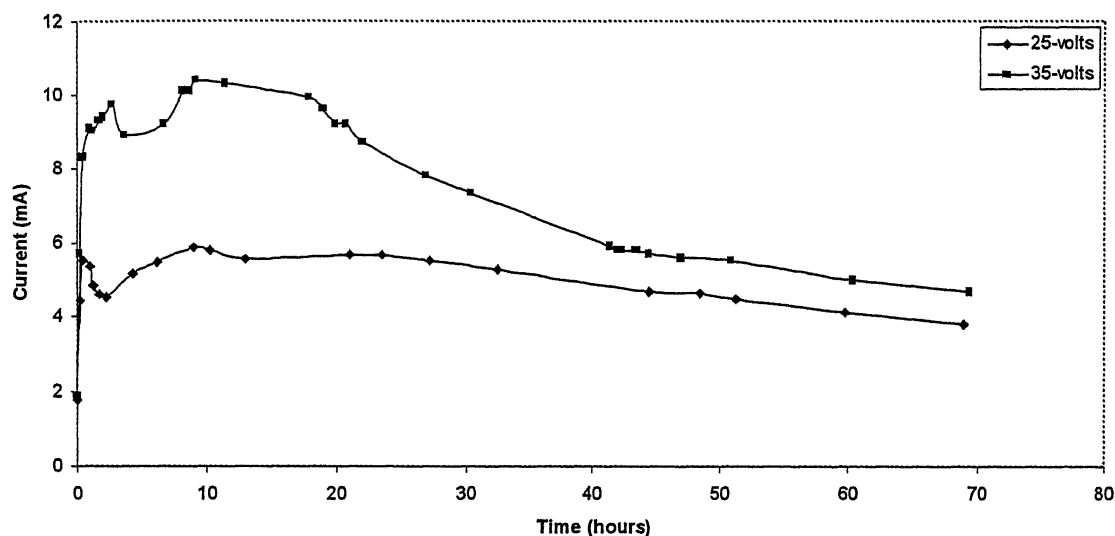


Fig 3.1 Variation of Current with Time in Kanpur soil (V=25 and 35-volts)

3.2 Experimental set up

Experiments for electroremediation has been carried out using one-dimensional set-up. One-dimensional set-up means the voltage is applied along one direction for the removal of chromium. The fluxes are unidirectional that's why the set-up is so called. In this section the whole experimental procedure for the experiments will be discussed.

One Dimensional Set-up

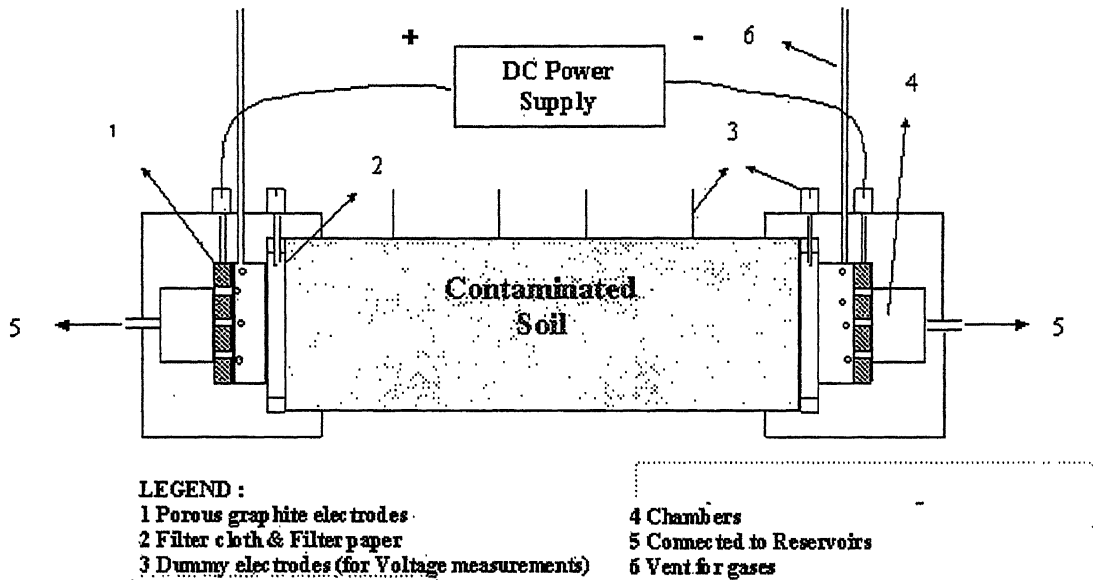


Fig 3.2 Schematic diagram of the One-Dimensional set-up

Fig. 3.2 is a schematic sketch of the 1-D experimental apparatus. A cylindrical Perspex tube, 15.25 cm long and 3.81 cm in diameter, was used to house the contaminated soil. Two Perspex caps containing the graphite electrodes 4 cm in diameter and 1 cm in thickness and liquid compartments 4.8 cm and 5.8 cm in diameter at different 2 sections, with provision for gas venting were screwed on to both ends of the Perspex cylinder. Holes were drilled in the graphite electrodes for (i) the passage of ions from the soil to electrode compartments and (ii) to accommodate bulk electrolyte flow by electroosmosis. In our earlier set-up, the soil was in direct contact with the electrodes. However, blockage of electrode holes by electrolytically generated gases, at the soil-electrode interface, prevented the passage of ions from the soil into the electrode (anode) compartment as well increased the resistance. To overcome this deficiency, the soil was separated from the electrodes by pushing the electrodes into the compartments and the vent was kept in front so that the gas bubbles generated can escape from vent. A porous canvas cloth and filter papers, in turn, supported the soil. The ends of the two Perspex caps were connected to two reservoirs, which served as an “electrolyte source” for

electroosmosis. Four dummy electrodes were inserted in the soil to determine the voltage distribution along the length of the reactor. Inter distance between any two dummy electrode was 2.1 cm.

3.3 Experimental Procedure

Initial conditions, such as dry densities, porosity, degree of saturation, and soil pH were all most similar in all cases. Total experimental process consists of different experimental steps. These are (1) Potassium Dichromate solution (Influent) preparation (2) Fitting the experimental set up (3) Soil preparation & compaction (4) Monitoring of current, voltage & electroosmotic flow rate with time (5) Sampling of solution with time for kinetics study (6) Soil extrusion (7) Cr(VI) analysis.

3.3.1 Influent Preparation

Here for the source of Cr(VI) the solution of $K_2Cr_2O_7$ has been taken as a source of Cr. The solution for the soil contamination should be prepared as such to get the required concentration of Cr(VI) in the soil. For 500mg/Kg of dry soil the calculated weight of $K_2Cr_2O_7$ taken was 0.4239 gram in 300 grams of dry soil. Then to get the required moisture content in the soil $K_2Cr_2O_7$ was added to double distilled water so that the moisture in soil should be 15 percentage i.e. for 300 grams soil water added is 45ml and in Kaolin 35 percentage moisture is achieved by adding 70ml water in 200 grams dry kaolin. The solution is prepared by dissolving $K_2Cr_2O_7$ with the distilled water.

3.3.2 Fitting the experimental set up

The set up used for previous experiment were first cleaned thoroughly with tap water to remove the Cr remained stick to the set up. Rings were then covered with canvas cloth with gum to give support to the slurry material. Both electrodes and rings were tightened with steel screws. Above the canvas cloth a same size of filter paper was placed to stop

the movement of fine soil particle into the chamber. The screws were tightened with washers to avoid leakage of water.

3.3.3 Soil Preparation and Compaction

The composition of Kanpur soil and Kaolin are as given in Table 3.2 and 3.3 respectively.

Table 3.2 Composition of Kanpur Soil

Composition of Kanpur Soil	
Mn	0.03%
Zn	0.01%
Cr	0.04%
Fe	3.83%
Co	0.02%
Ni	0.003%

Table 3.3 composition of LOBA Kaolin

Composition of Loba Kaolin	
Heavy metals as Lead	0.002%
Chloride	0.02%
Sulphate	0.05% (max)

Soil is mixed thoroughly with requisite volume of $K_2Cr_2O_7$ solution to achieve the desired Cr(VI) concentration of 500 mg/kg soil. The resulting slurry, with a 60-65 % degree of saturation, was compacted in the Perspex tube by applying 17.34 kg static load from the top with other end closed. Loading time for each layer of compaction was 10

minutes, after each layer of compaction slurry was scratched with a wire to maintained uniformity with the 2nd layer of compaction. Compaction was completed after 5 layer of compaction. After that both ends were capped with the caps. -ve reservoir and +ve reservoir were connected with the -ve chamber and +ve chamber respectively by polymer tubes. To avoid hydraulic gradient the two chambers were filled with distilled water and a level up to 50 in both the reservoirs were filled.

3.3.4 Measurements of Current, Voltage and Electroosmotic Flow

A constant DC voltage power supply was connected to the graphite electrode and operated for 72 hrs. Electroremediation experiments were carried out at 25 and 15 volts in a tube of length 15 cm and 12.5 and 7.5 V experiments were carried out in 7.5cm tube to study the scale up criteria for the optimum electrode spacing. Voltage drop across the soil were observed from section to section. There are dummy electrodes placed across the soil to observe voltage drop in various section the voltage as well as current are measured with multimeters. Due to electroosmosis the water level in both the reservoirs changes with time. So to avoid hydraulic head driven flow, levels in the reservoirs were continuously adjusted to ensure that difference in electrolyte levels never exceeded 10 cm³.

3.3.5 Sampling

4 ml samples were taken from time to time to analyse kinetic of the process from the chambers and reservoirs depending on in which direction chromium have come in. Samples were taken 3-5 times during the 72 hours experiment, generally at least once a day. The analysis gives the idea at which the Cr is removed.

3.3.6 Extrusion

After 72 hours the slurry material was extruded by applying constant extruding force using a screw feeder mechanism, from the Pyrex tube. The pH profile of the soil was first measured using a universal pH paper.

3.3.7 Cr(VI) Analysis

Each sections of the soil were weighed and analysed for Cr(VI) and total chromium. Each section were first thoroughly mixed. To determine residual Cr(VI) in soil, some portion of samples from each soil sections were mixed in conical flasks containing double distilled water and stirred for 2 hrs in a shaker. After 2 hrs shaking of the slurry material was centrifuged in a centrifugal instrument, at that time all soil particle settled down and soil particles free chromium solution was used for Cr(VI) analysis. Soil particles settling depends on the pH of the solution, in alkaline solution soil particles is not settled at that time 2-3 drops of concentrated H_2SO_4 was added to settled down the soil particles. The resulting solution was analysed for Cr(VI) colorimetrically using US-EPA method. Measured quantity of Cr(VI) solution was taken in volumetric flask containing 2 pH solution to achieve desire Cr(VI) concentration and pH .05-2 PPM and 1-3 respectively in the volumetric solution. 2-3 drops of 1,5 diphenyl carbazide solution was added as indicator to develop violate colour for UV analysis. Diphenyl carbazide solution was prepared by homogeneous mixing of 0.25 gm diphenyl carbozide in 50 ml acetone.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Experimental results

The primary objective of this investigation is to know whether galvanostatic or potentiostatic supply should be used for efficient removal of Cr(VI) from different kinds of soils. Experiments were carried out with different constant DC voltage and constant DC current supply. Two types of soils were used in the study: Kanpur soil and kaolin

4.2 Kaolin

4.2.1 Predominant mechanism for material transport

The movement of water soluble Cr(VI) ion is governed by two predominant mechanisms, electroosmosis and electromigration. The Cr(VI) ion exists as oxyanions hydrochromate HCrO_4^- , dichromate $\text{Cr}_2\text{O}_7^{2-}$ and chromate CrO_4^{2-} in water. These oxyanions are soluble in wide range of pH. As the nature of the whole ion is negative so they move towards anode side.

Soil typically has a negative surface charge. To balance this charge a row of cations, such as hydrogen, sodium, potassium, line up along the soil particle surfaces. Under the influence of a DC field, the rows of cations on the soil particle surfaces start migrating towards the cathode by electrical attraction. The movement of this cationic layer drags the pore fluid with it. With the pore fluid movement Cr present in the pore fluid also get dragged with that towards cathode. So the case where electroosmosis is predominant over electromigration there the Cr gets accumulated in the cathode chamber. In case of kaolin it has been observed that the Cr gets accumulated in the cathode chamber, which conforms that the predominant driving flux for the removal of Cr is electromigrating flux.

4.2.2 Kinetics of removal of Cr from kaolin

4.2.2.1 Comparison between 10mA and 15-volts experiment for kaolin

Fig. 4.2 shows the rate of ERM of chromium from kaolin at (i) 15-volts and (ii) 10 mA. By comparing the kinetics plot shown in Fig 4.2 it can be seen that the percentage Cr removed under both potentiostatic and galvanostatic conditions are similar after 72 hours (see Table 4.1). However, the kinetics of electroremediation is different for the two cases. In case of the 15-volts experiment the rate in first few hours is greater than the 10mA experiment and then it falls. But in the 10mA experiment the rate of removal is approximately constant. Fig. 4.18 shows that electroosmotic flow is also greater under constant voltage conditions. It is interesting to note that under potentiostatic conditions electroosmotic flow reduces drastically after 40 hours. However, electroosmotic flow continues to increase and becomes greater than electroosmotic flow under potentiostatic conditions after 60 hours.

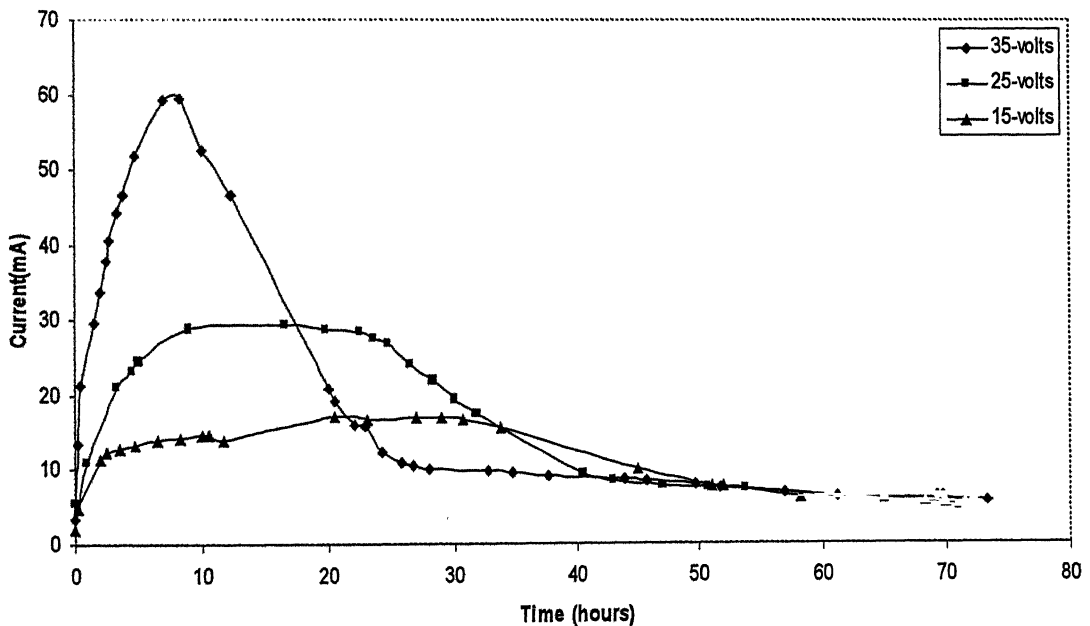


Fig. 4.1. Variation of Current with Time for Kaolin (V=15, 25 and 35-volts)

Table 4.1 Percentage of Cr removed after 72 hours at different operating conditions

Operating parameters	Percentages of Cr removed after 72 hours (%)
35-volts	46.7
25mA	89.6
25-volts	30.3
15mA	31.0
15-volts	18.2
10mA	18.7

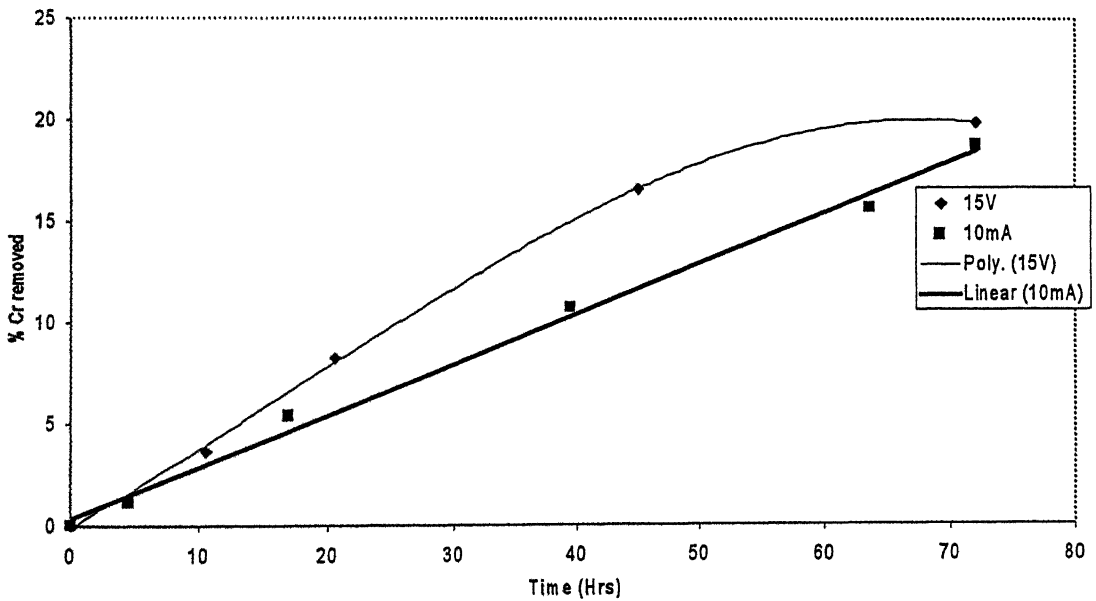


Fig 4.2. Electroremediation of chromium as a function of Time for Kaolin 15-volts and 10mA experiments

In electroremediation, the net flux of chromium is given by:

$$N_{Cr} = -u_{Cr} C_{Cr} \nabla \phi + v C_{Cr} \quad (1)$$

Where,

$\nabla \phi$ = Potential gradient.

C_{Cr} = Concentration of Cr(VI)

u_{Cr} = Mobility of Cr(VI)

v = Electroosmotic velocity $\propto \zeta \nabla \phi$

ζ = Zeta potential

The terms on the RHS of equation 1 represent flux due to electromigration and electroosmosis respectively. u_{Cr} is a function of ion size, concentration of Cr(VI), and ionic strength of the solution. Assuming that u_{Cr} does not change appreciably with time, electromigration is proportional to $\nabla \phi$. Electroosmosis is proportional to the product of ζ and $\nabla \phi$. However, ζ is a function of pH, which, in turn, is intimately related to $\nabla \phi$ across the soil. Hence evolution of the $\nabla \phi$ profile in soil should have a major bearing on the kinetics of chromium removal. Assuming that potential gradient across kaolin is linear, the potential drop, $\Delta \phi$, measured across different sections of the soil, should be proportional to $\nabla \phi$. Consequently, the reasons for the difference in the electroremediation kinetics between the 15-volts and 10mA cases can be determined by analyzing the voltage distribution plots shown in Figs. 4.3 and 4.4. In the galvanostatic experiments, the variation of total voltage with time is given in Fig. 4.17.

Fig. 4.3 shows that the voltage drop in section 1, adjacent to the cathode, increases rapidly after approximately 30 hours, representing more than 60% of the total voltage, (shown in Fig 4.4). Sanjay et. al. [31] have attributed the high voltage drop in section 1 as the rate controlling step in the electroremediation of Cr(VI) from kaolin. The high voltage drop in section 1 reduces the driving force for both electroosmosis and

electromigration and is thus responsible for the decrease in the kinetics of electroremediation of chromium.

Hamed et al. [5] attributed the high voltage drop near the cathode to the depletion of ion carriers due to acid base neutralization. Fig. 4.15 shows that more than 90% of the entire soil section becomes acidic at the end of electroremediation. pH measurements also showed that kaolin close to the cathodic end was basic. In fact, experiments conducted by Sanjay et. al. [27] at 25 volts show that the basic and acid fronts meet after approximately 20 hours, which happens to be the time after which the voltage drop in section 1 starts increasing. Consequently, acid-base neutralization appears to be the rate-controlling step in the electrochemical cleaning of chromium-contaminated kaolin.

Fig. 4.5 shows that under galvanostatic conditions, the voltage drop in all the five sections are almost constant, and therefore the driving force for electromigration remains similar. However, electroosmotic flux should decrease because the motion of the acid front decreases ζ . Consequently, the net flux of Cr(VI) into the anode chamber, should at least remain constant, if not increase. However, it is interesting to note that the increase in voltage drop in section 1 does not adversely affect the electroremediation of Cr(VI), as in the 15-volts experiment. The magnitude of current in electroremediation represents the flux of all ionic species in the pore fluid. In the 15 V experiment, the current is high for first 30 hours shown in Fig 4.1, around 15mA so the removal rate is high in this time after which current becomes extremely small, 5mA. Hence the relatively higher current of 10mA in the galvanostatic experiment literally “forces” the ions, including Cr(VI) from kaolin into the anode chamber. Or, in other words, the high current leads to an overall increase in the magnitude of voltage drop in all sections as the resistance increases with time due to neutral layer formation, as shown in Table 4.2. However, the penalty for the higher Cr(VI) removal rate under galvanostatic conditions is levied in the form of higher voltage, and therefore high energy consumption.

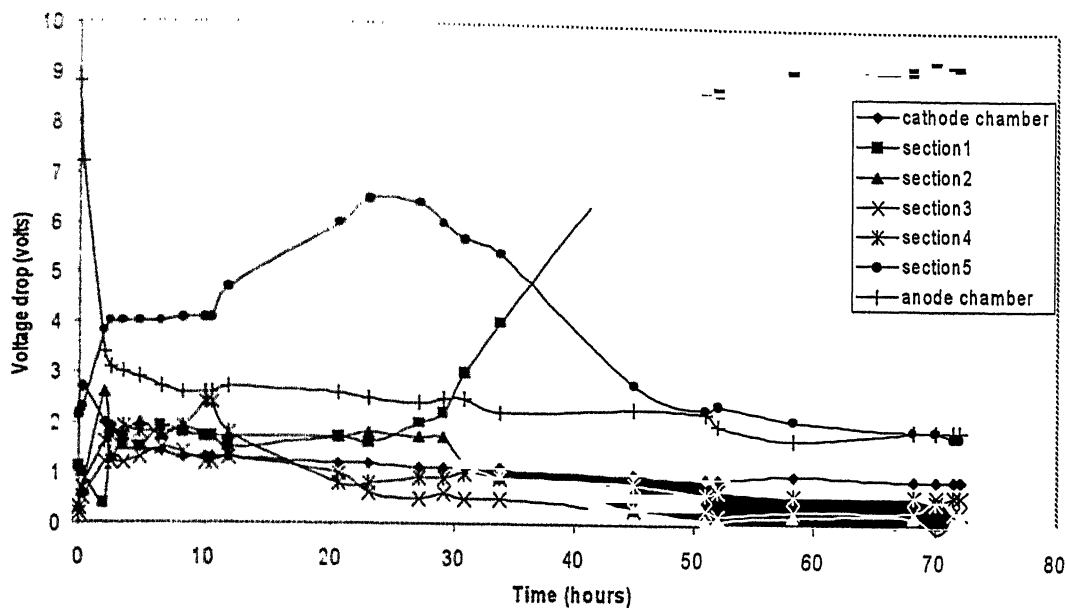


Fig 4.3. Voltage drop at different sections of Kaolin as a function of Time (V=15-volts)

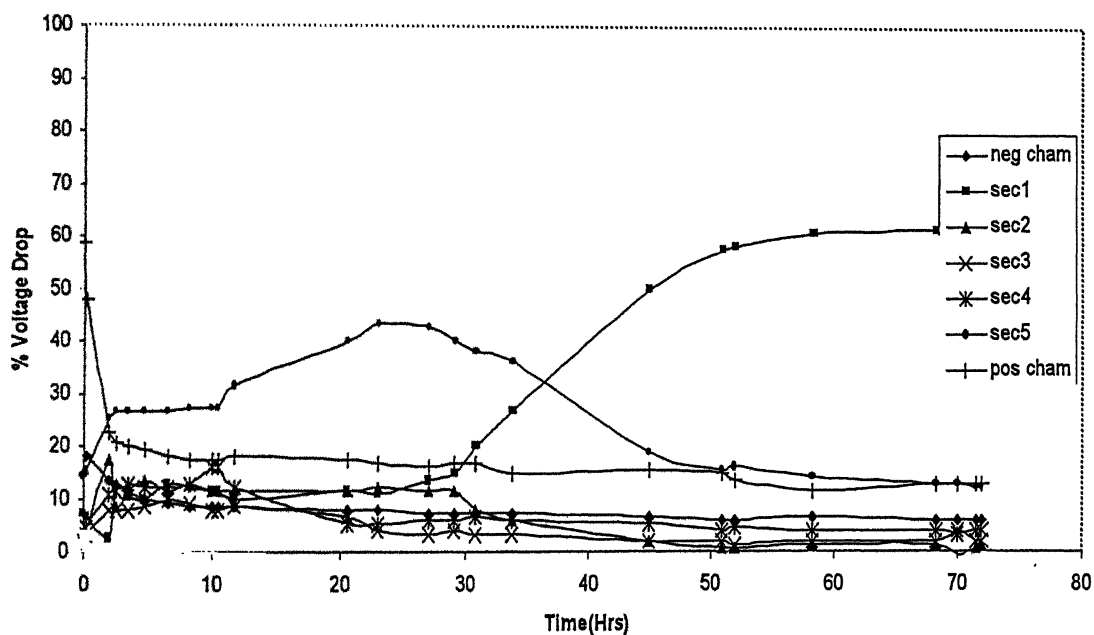


Fig 4.4. Percentage voltage drop at different sections of Kaolin as a function of Time (V=15-volts)

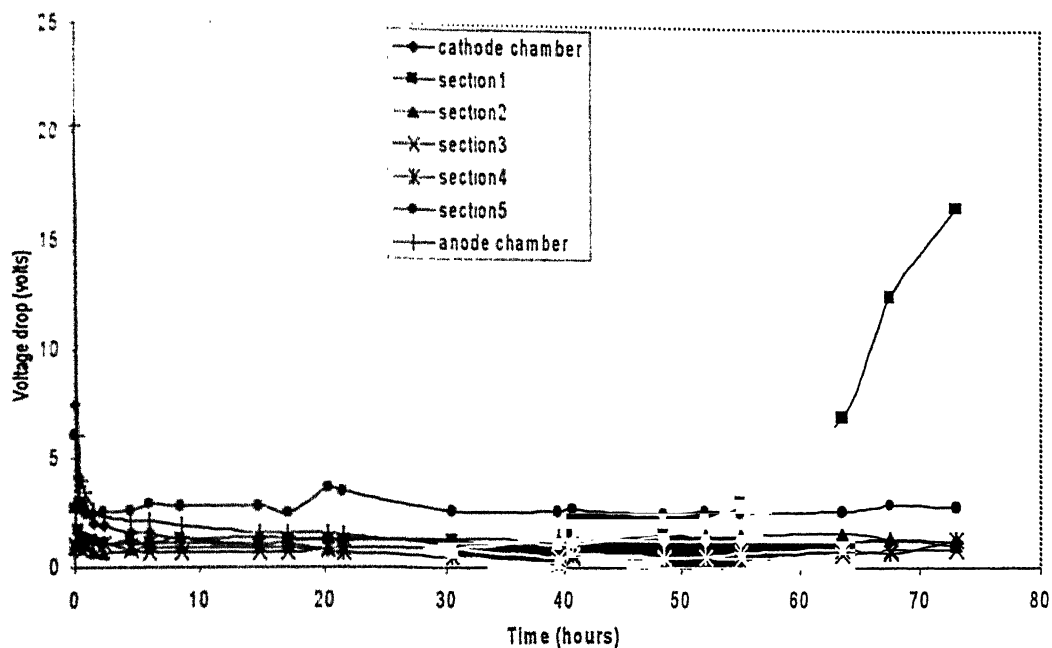


Fig 4.5. Voltage drop at different sections of Kaolin as a function of time (Current=10mA)

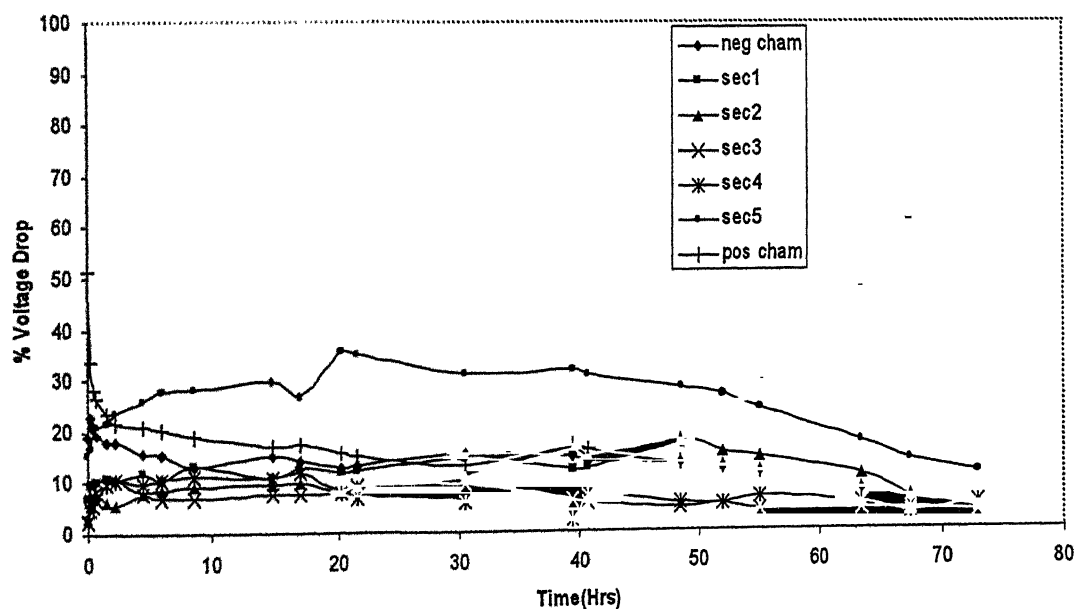


Fig 4.6. Percentage voltage drop at different sections of Kaolin as a function of time (Current=10mA)

Table 4.2 Voltage Drop Comparison between 10mA and 15-volt experiment

Time		Cathode Chamber	Section1	Section2	Section3	Section4	Section5	Anode Chamber
10hrs	10mA	1.3	1.3	0.9	0.7	1.1	2.8	1.9
	15-volts	1.3	1.7	1.7	1.2	2.4	4.1	2.6
20hrs	10mA	1.3	1.2	0.8	0.8	0.8	3.6	1.6
	15-volts	1.2	1.7	1.7	1	0.8	6	2.6
30hrs	10mA	1.3	1.2	0.9	0.8	0.5	2.6	1.1
	15-volts	1.1	3	1.2	0.5	1	5.7	2.5
50hrs	10mA	1.2	2.2	1.5	0.5	0.5	2.6	1.2
	15-volts	0.9	8.6	0.1	0.3	0.6	2.3	2.2
70hrs	10mA	1.2	16.7	1	0.8	1.3	2.8	1.2
	15-volts	0.9	9.3	0.1	0.6	0.5	1.9	1.9

4.2.2.2 Comparison between 15mA and 25-volts experiment for kaolin

The removal kinetics of chromium from kaolin for the cases of 25-volts and 15mA are shown in Fig 4.7. From this figure it is clear that the percentage chromium removed after 72 hours for both the cases are almost equal but the rate is different as in the previous case of 15-volts and 10mA experiments. In case of 15mA experiment the removal rate stays almost constant but in case of 25-volts the decreases after 30 hours. The reasons for the difference in kinetics between the 15 mA and 25 V experiments are similar to those in the 10 mA and 15 V experiments, which is evident when (i) Figs. 4.8, 4.10 is compared with Figs. 4.3, 4.6 and (ii) Table 4.3 is compared with Table 4.2.

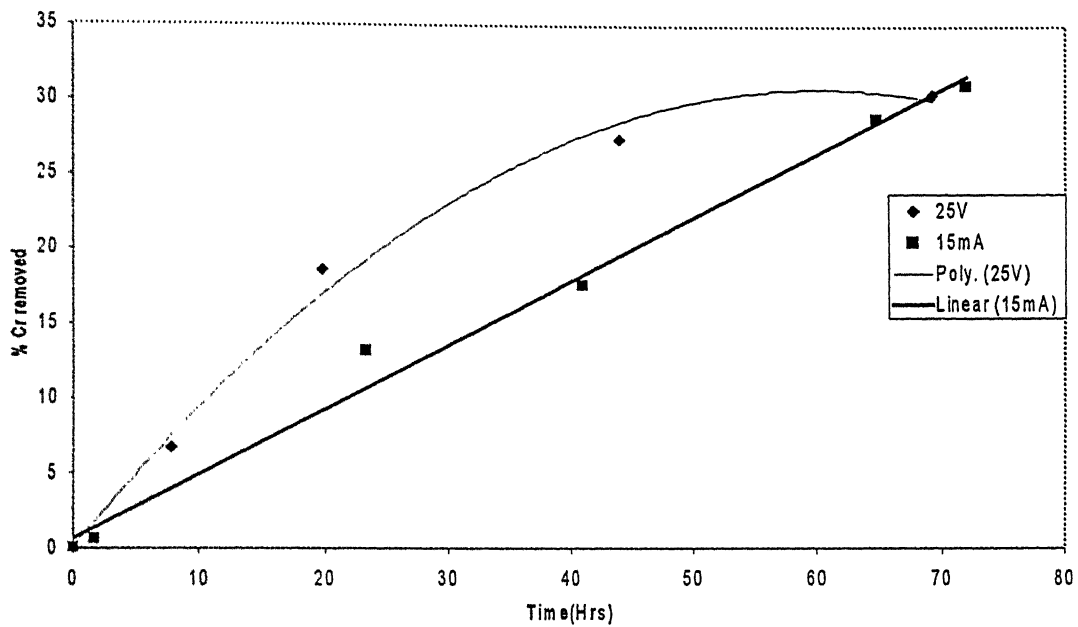


Fig 4.7. Comparison of percentage of Cr removed with Time for kaolin experiments (25-volts and 15mA)

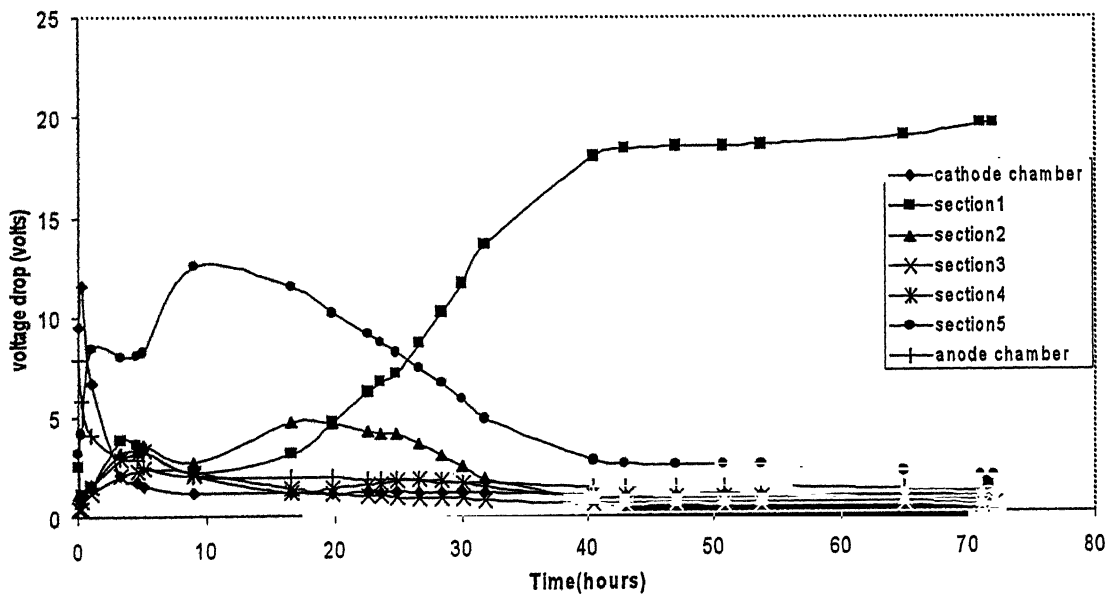


Fig 4.8. Voltage drop at different sections of Kaolin as a function of Time (V=25-volts)

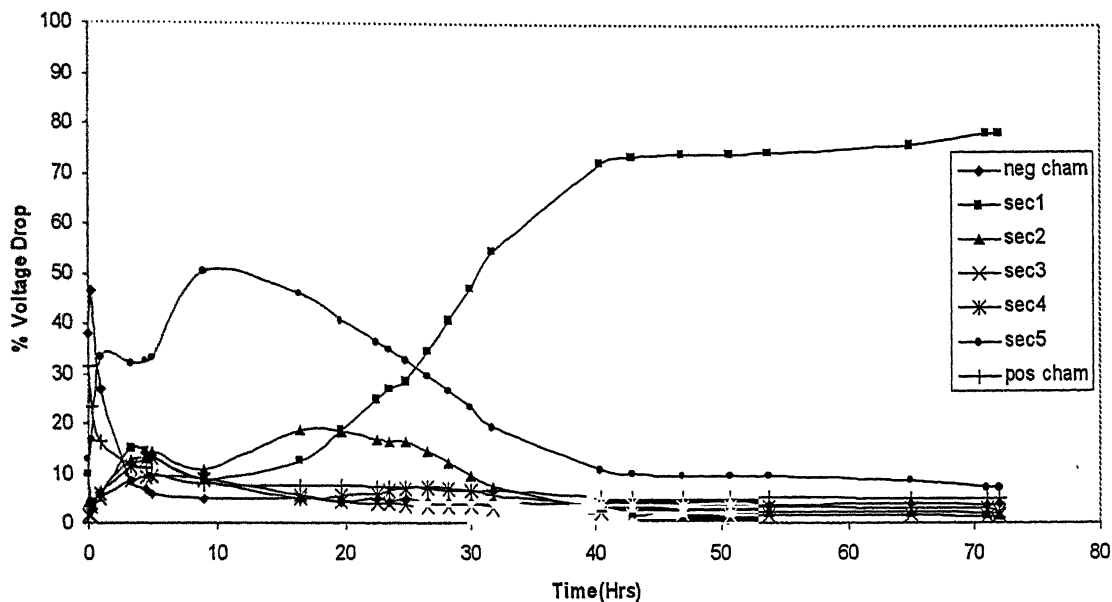


Fig 4.9. Percentage voltage drop at different sections of Kaolin as a function of Time (V=25-volts)

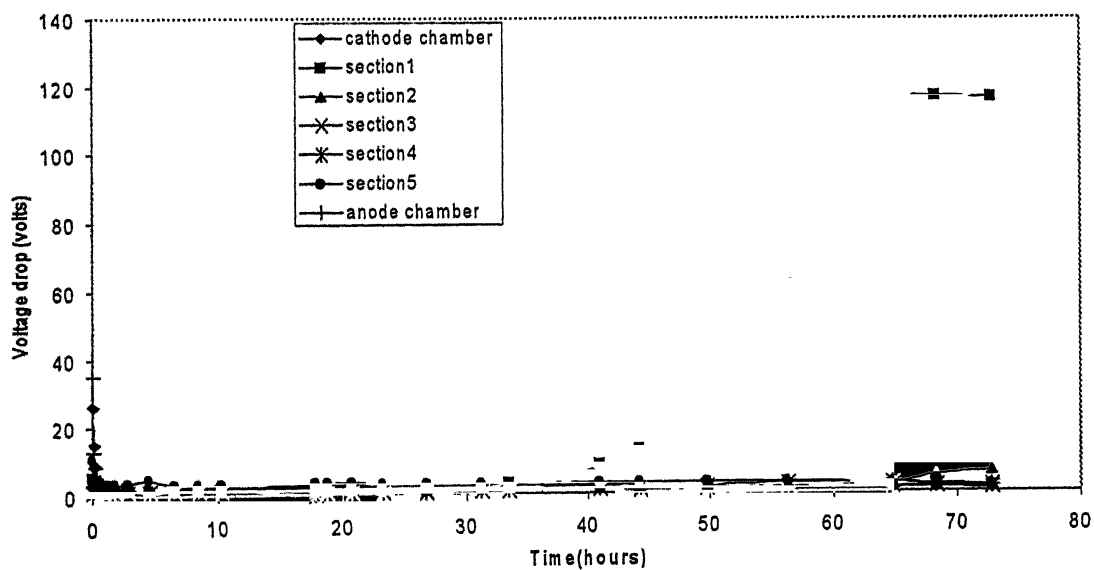


Fig 4.10. Voltage drop at different sections of Kaolin as a function of Time (Current=15mA)

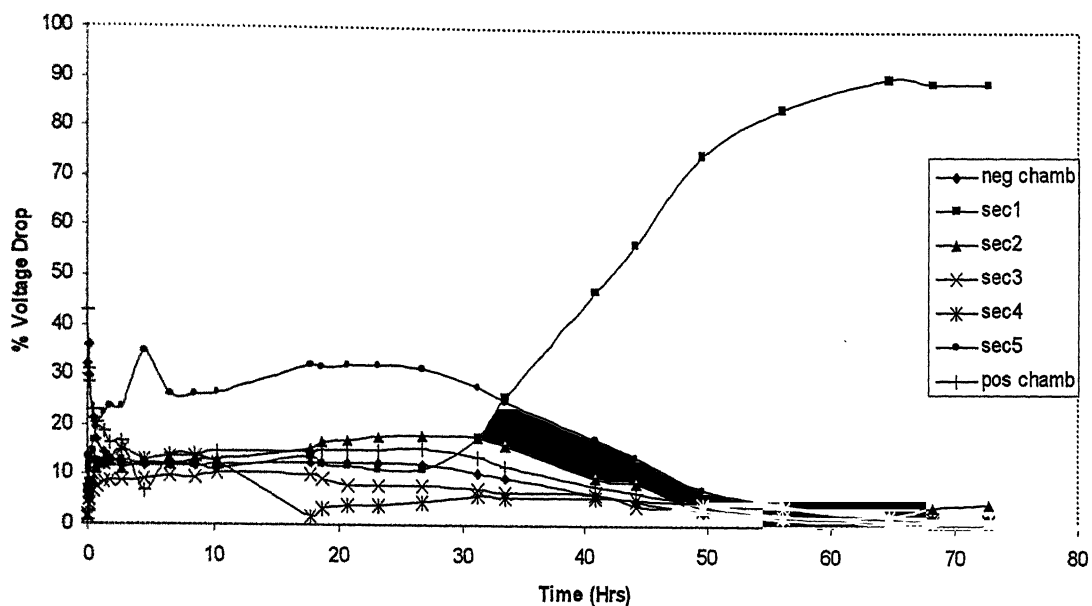


Fig 4.11. Voltage drop at different sections of Kaolin as a function of Time (Current=15mA)

Table 4.3 Voltage Drop Comparison between 15mA and 25-volt experiment

Time		Cathode Chamber	Section1	Section2	Section3	Section4	Section5	Anode Chamber
10hrs	15mA	1.4	1.3	1.52	1.22	1.46	3.09	1.72
	25-volts	1.2	2.2	2.7	2.2	2.1	12.6	2
20hrs	15mA	1.3	1.23	1.77	0.8	0.4	3.33	1.55
	25-volts	1.1	4.7	4.6	1.1	1.4	10.2	1.9
30hrs	15mA	1.2	2	2	0.8	0.65	3.15	1.54
	25-volts	1.1	11.7	2.4	0.8	1.6	5.8	1.6
50hrs	15mA	1.1	30.7	1.4	1.3	1.8	3	1.7
	25-volts	1	18.5	0.6	0.4	0.8	2.4	1.3
70hrs	15mA	0.9	116.4	6	1.2	1.8	2.1	1.6
	25-volts	0.9	19.6	0.5	0.3	0.7	1.8	1.2

4.2.2.3 Comparison between 25mA and 35-volts experiment for kaolin

The kinetics of chromium removal in case of 25mA and 35-volts are shown in Fig 4.12. From this Fig it is clear that after 72 hours the total percentage of chromium removed from kaolin in case of 25mA experiment is 89%, compared to 46% in the 35-volts experiment. The kinetics of the galvanostatic (25 mA) experiment is always greater than the potentiostatic experiment (35 V), a phenomenon that is at variance with the 10 mA – 15 V and 15 mA – 25 V experiments.

In case of 35-volts experiment the same thing happens as in case of 25-volts experiment. The total voltage drops down after 20 hours to 10mA. This is due to the initial high current. Due to high current the hydrogen front moves much faster towards the cathode side and the neutral layer is formed quickly after 20 hour near the cathode in section 1, compared to hrs and hrs in the 15 V and 25 experiments respectively. So in section 1 the voltage drops maximum around 80 percentage¹ as shown in Fig 4.13 and 4.14. In all other sections, the voltage drop, and hence the driving force for the transport of Cr(VI), is much lower. Consequently, the formation of the neutral layer is the reason for the lower rate of removal of chromium, as in the 15 V and 25 V experiments.

Fig 4.19 shows the electroosmotic flow rate in case of 15mA and 25-volts experiment. Here it can be observed that in case of 25-volts experiment the rate is high initially but after 60 hours the rate in case of 15mA is high due to high total voltage drop across the tube.

¹ Due to the error of the instrument the experiment couldn't be operated at 25mA after 60 hours and it fell down to 17mA after 60 hours. Hence the voltage drop in section 1 should be greater than 80%

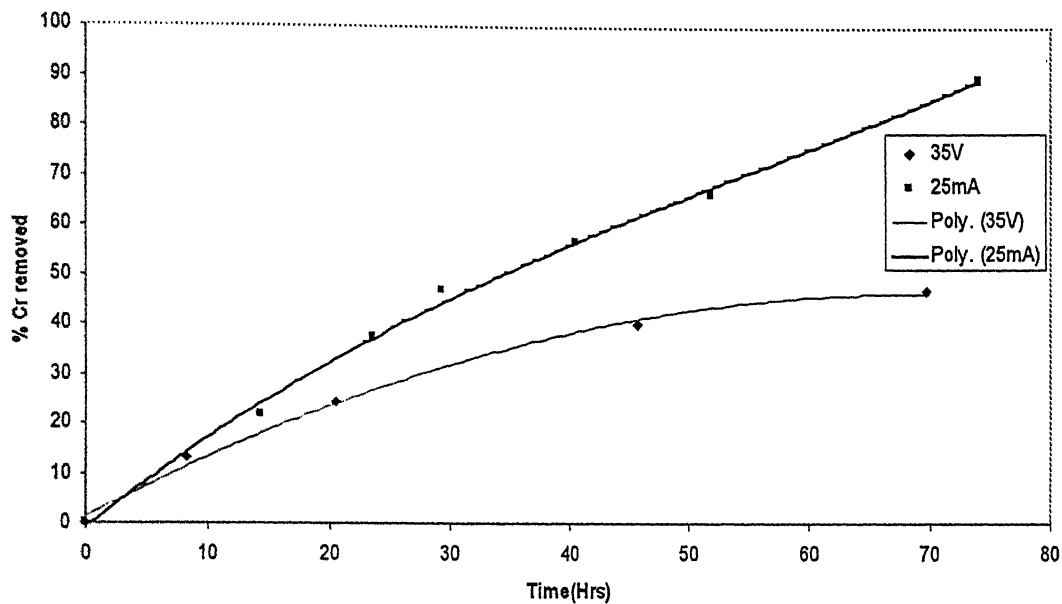


Fig 4.12. Comparison of Percentage Cr removed with Time for kaolin (35-volts Vs 25mA)

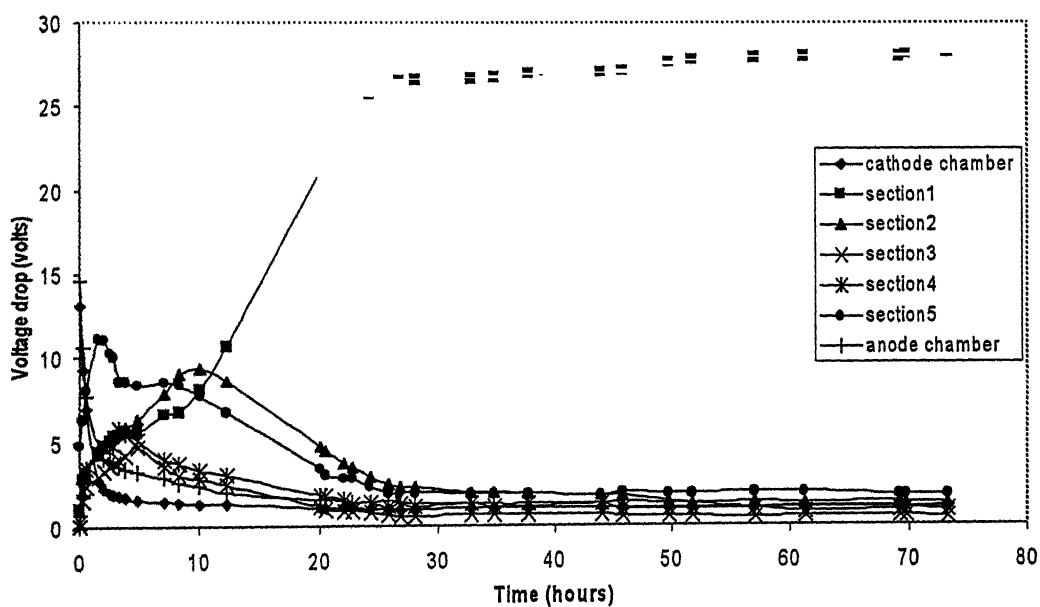


Fig 4.13. Voltage drop at different sections of Kaolin as a function of Time (V=35-volts)

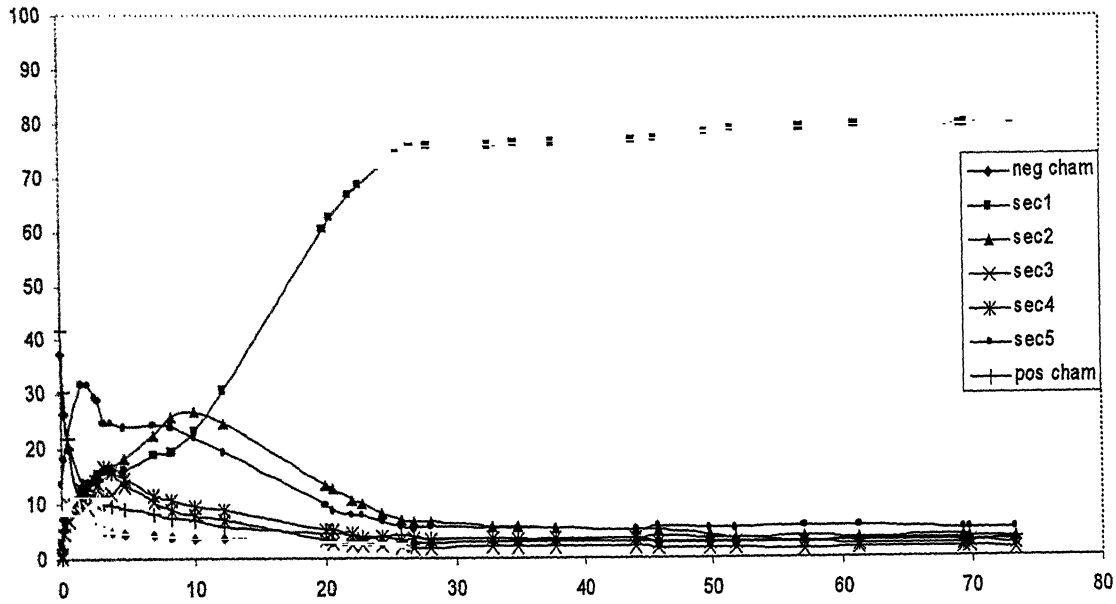


Fig 4.14. Percentage voltage drop at different sections of Kaolin as a function of Time (V=35-volts)

In case of 25mA experiment the acid-base neutralization occurs after 30 hours after which the voltage drop in section 1 increases. As the current is high and stays constant through out 72 hours the voltage drop in every section increases after 35 hours due to increase in resistance as shown in Fig 4.16 and 4.17. The increase in percentage removal in case of 25mA experiment can be better explained from Table 4.4. From this table it is clear that after 40 hours the voltage drop in all sections is high and also in these sections the distribution of voltage is uniform. This is the reason why the removal is high in case of 25mA experiment.

If the electroosmosis plot (shown in Fig 4.20) is seen then it clear that at first the electroosmosis in case of 35-volts is high but the rate gradually falls but in case of 25mA experiment the electroosmosis rate is slower initially and increases latter. This is due to the high total voltage drop (shown in Fig 4.17) after 40 hours.

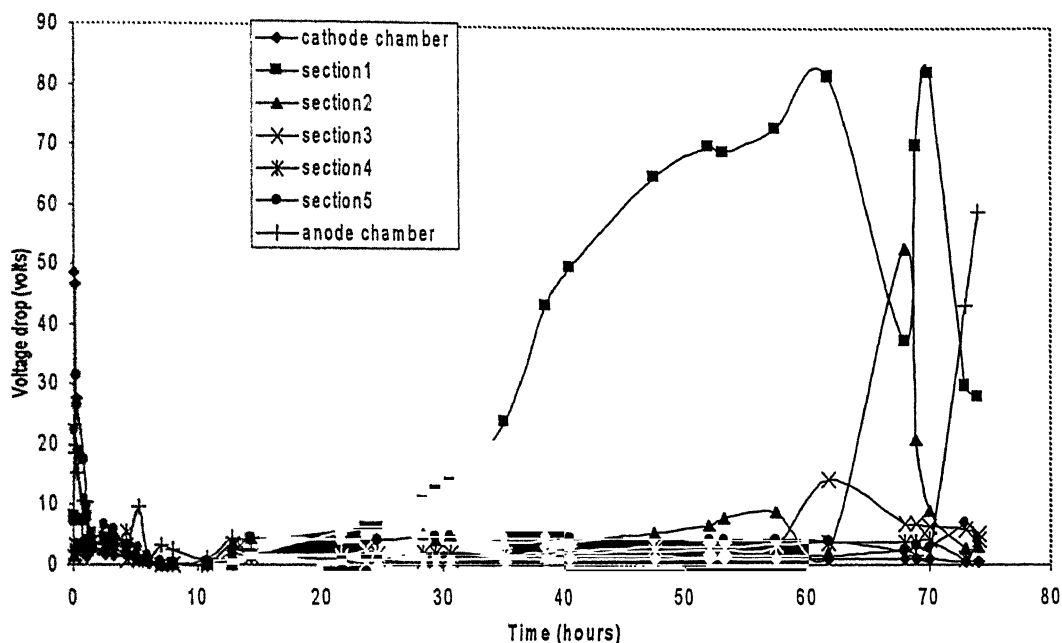


Fig 4.15. Voltage drop at different sections of Kaolin as a function of Time (Current=25mA)

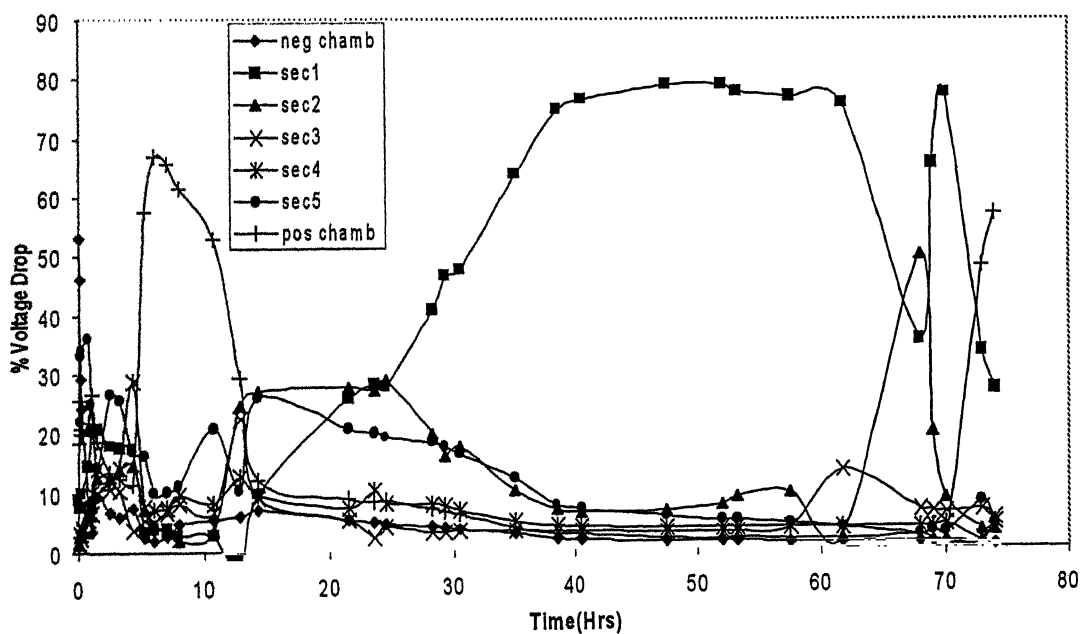


Fig 4.16. Percentage voltage drop at different sections of Kaolin as a function of Time (Current=25mA)

Table 4.4 Voltage Drop Comparison between 25mA and 35-volt experiment

Time		Cathode Chamber	Section1	Section2	Section3	Section4	Section5	Anode Chamber
10hrs	25mA	0.8	1.2	1.7	2.7	3.9	7	14.8
	35-volts	1.3	8.1	9.4	2.8	3.3	7.7	2.4
20hrs	25mA	1.1	5.4	5.8	1.1	1.5	4.3	1.8
	35-volts	1.1	21.2	4.7	1.2	1.8	3.4	1.6
30hrs	25mA	1	13.6	5	0.9	1.9	4.6	1.7
	35-volts	1.1	26.7	2	0.7	1.3	1.9	1.3
50hrs	25mA	1	70.2	6.7	2.5	3	4.3	1.3
	35-volts	1.1	26.9	1.9	0.7	1.3	1.9	1.2
70hrs	25mA	1	82.6	9.1	6.4	4.3	2.6	0.9
	35-volts	1.1	28.1	1.3	0.6	1	1.8	1.1

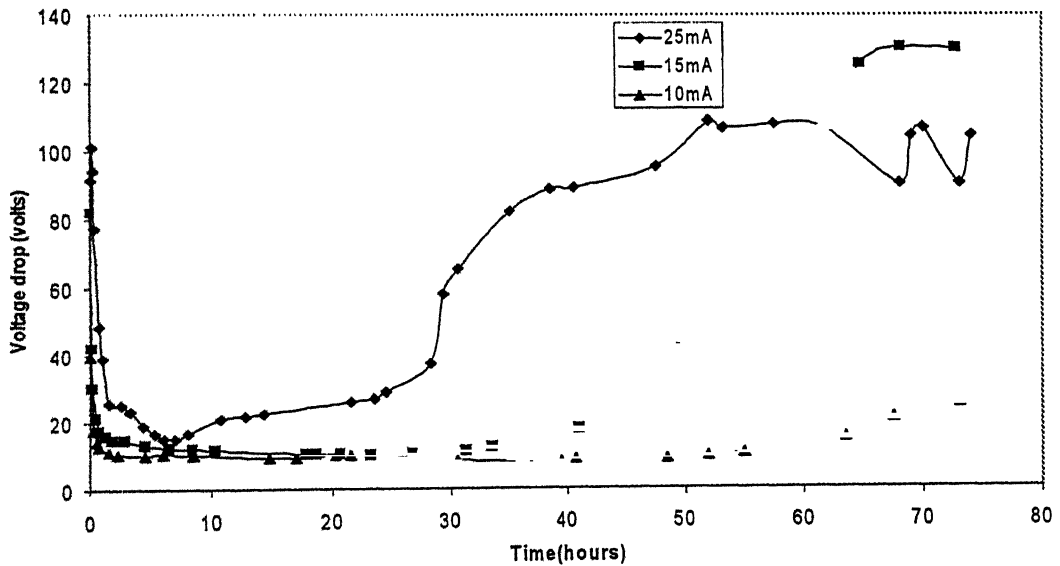


Fig 4.17 Total voltage drop across the tube for kaolin experiments (10, 15 and 25mA)

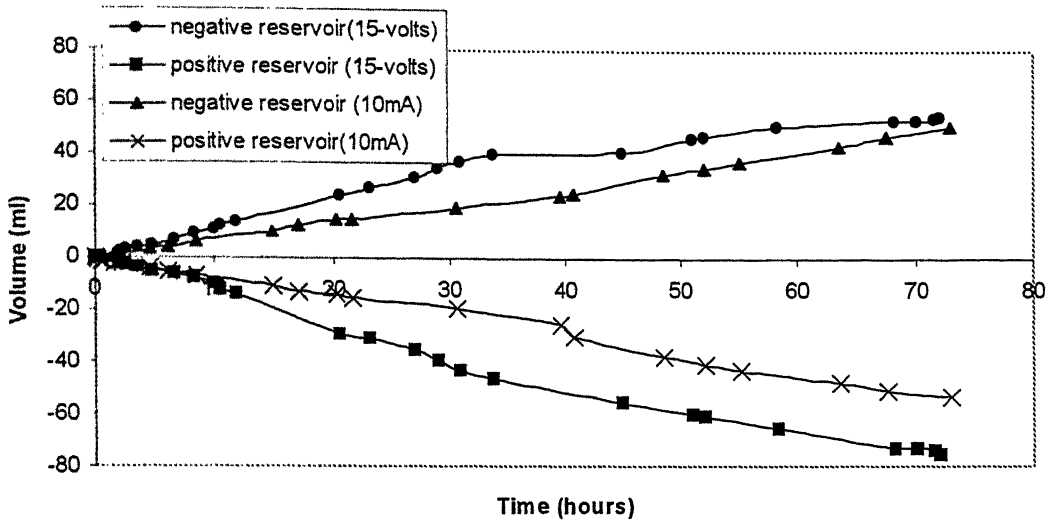


Fig4.18 Comparison of Electroosmotic flow between 15-volts and 10mA experiments for kaolin

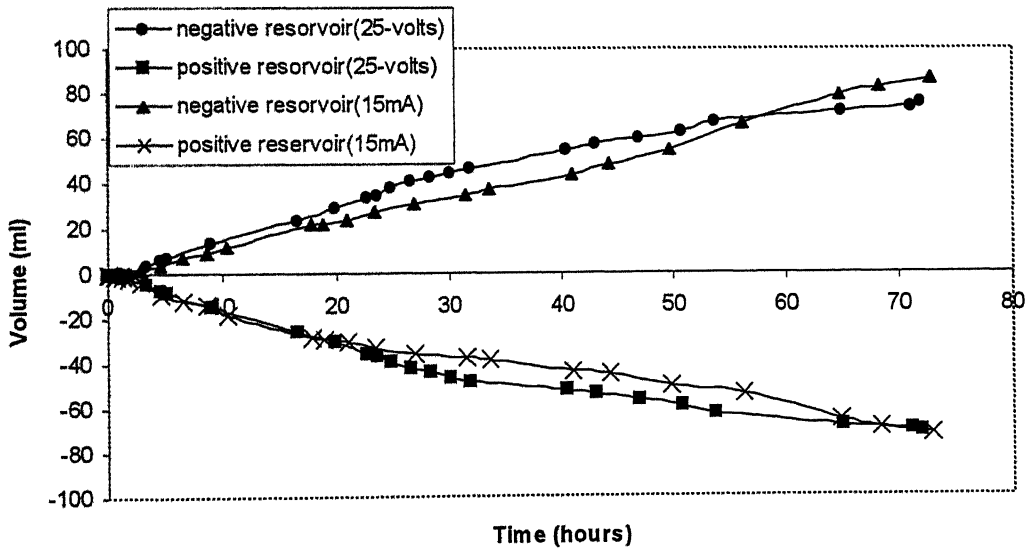


Fig4.19 Comparison of Electroosmotic flow between 25-volts and 15mA experiments for kaolin

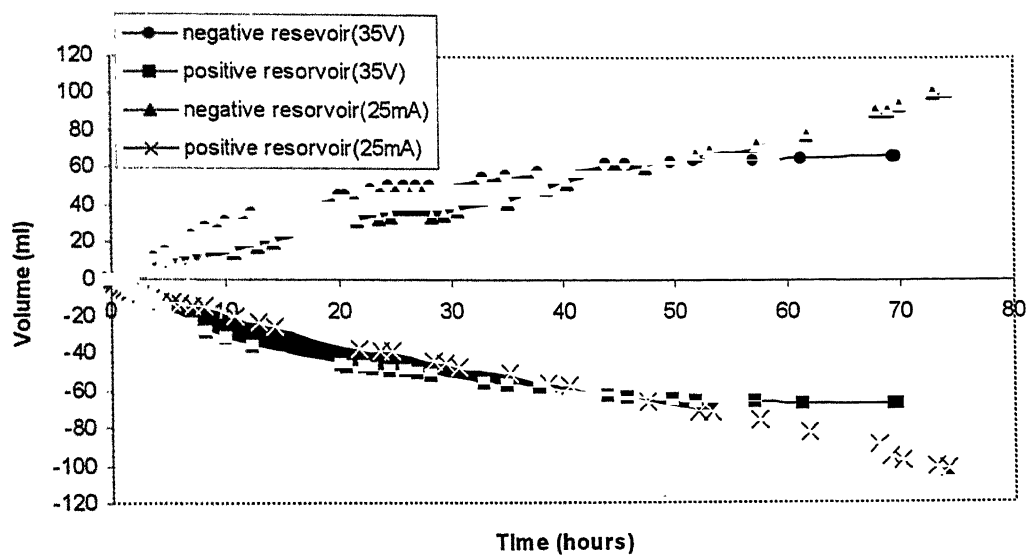


Fig4.20 Comparison of Electroosmotic flow between 35-volts and 25mA experiments for kaolin

4.3 Soil

4.3.1 Predominant mechanism for ion transport in Kanpur soil:

In case of Kanpur soil the chromium gets accumulated in the cathode chamber, which suggests that the predominant mechanism behind the transport of ion is electroosmosis. In case of Kanpur soil, although there is the presence of electromigrating force but the electroosmotic force is predominant over the electromigrating force.

4.3.2 Kinetics of remediation of chromium from Kanpur soil

4.3.2.1 Comparison between 5mA and 25-volts experiment for Kanpur soil

Fig 4.21 shows the kinetics of removal of chromium from Kanpur soil at galvanostatic experiment of 5mA and potentiostatic experiment of 25-volts. In case of potentiostatic experiment, it can be seen that after 40 hours, about 75 percentage of chromium is removed from the soil, whereas in case of galvanostatic experiment at 5mA the percentage chromium removed is much lower around 36 percentages. This clearly indicates the importance of the nature of the soil on the removal efficiency of chromium. It was pointed out earlier that kaolin is weakly acidic ($\text{pH} = 5.5$), while Kanpur soil is basic ($\text{pH} = 10$). This high remediation rate from Kanpur soil in case of 25 volts can be attributed to the higher electroosmotic flow rate shown in Fig 4.32, whereas in case of 5mA experiment it is much lower. This higher rate of electroosmotic flow in 25-volts case can be best explained from Fig 4.25, which shows the percentage voltage drop at different sections of the tube. From this figure it is clear that with time the voltage drop in section 5 is high and gradually the drop in voltage move towards the section 4 (shown in Fig 4.24 and values given in Table 4.6). This is obviously due to the high pH of Kanpur soil. The acid front generated at anode immediately gets neutralized near the anode at section 5 and due to higher mobility of hydrogen and continuous generation of hydrogen ion at anode the acid base neutralization gradually moves towards the other sections.

The higher voltage drop in section 5 of the Kanpur soil acts as an electroosmotic pump, drawing the electrolyte from the anode chamber and pumping it towards the cathode [31]. So the higher removal efficiency can be attributed to the electroosmotic pumping effect. This effect is higher in case of 25-volts experiment as the voltage drop across the tube in case of 5mA experiment is 15-volts approximately, from Fig 4.31.

Table 4.5 Percentage of chromium removed from Kanpur soil after 72 hours at different operating conditions

Operating parameters	Percentages of Cr removed after 72 hours (%)
35-volts	80
10mA	65
25-volts	75
5mA	40

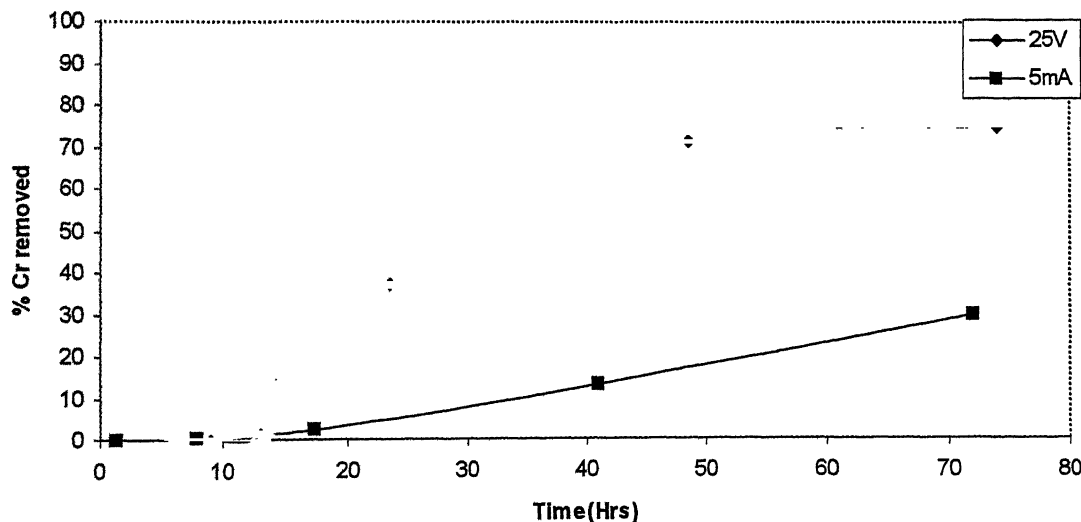


Fig 4.21 Percentage of Cr removed comparison between 5mA and 25-volts experiments (Kanpur soil)

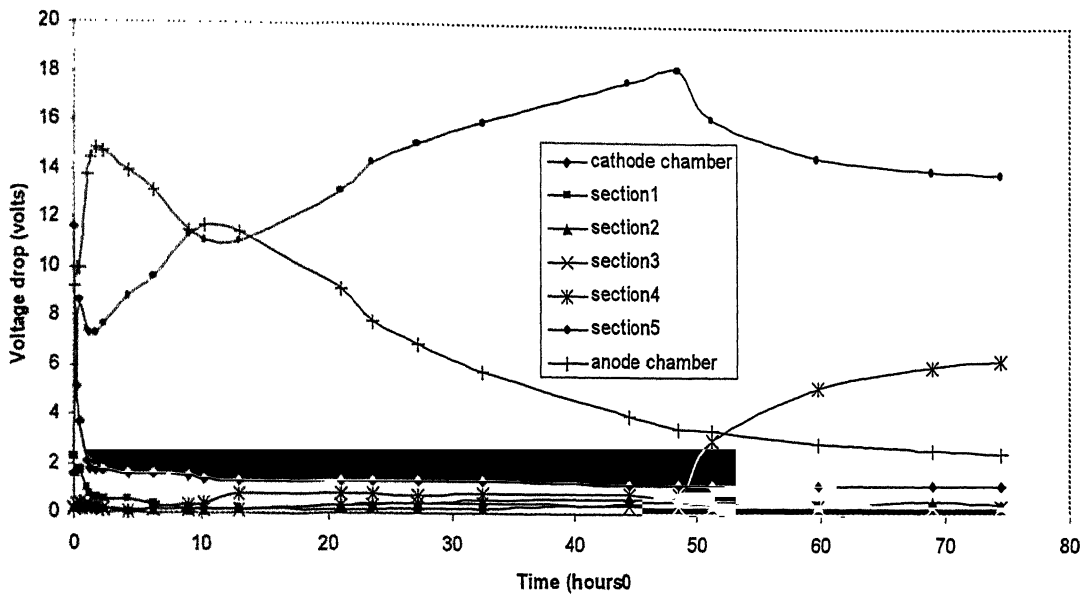


Fig 4.22 Voltage drop at different sections of the tube for Kanpur soil for 25-volts

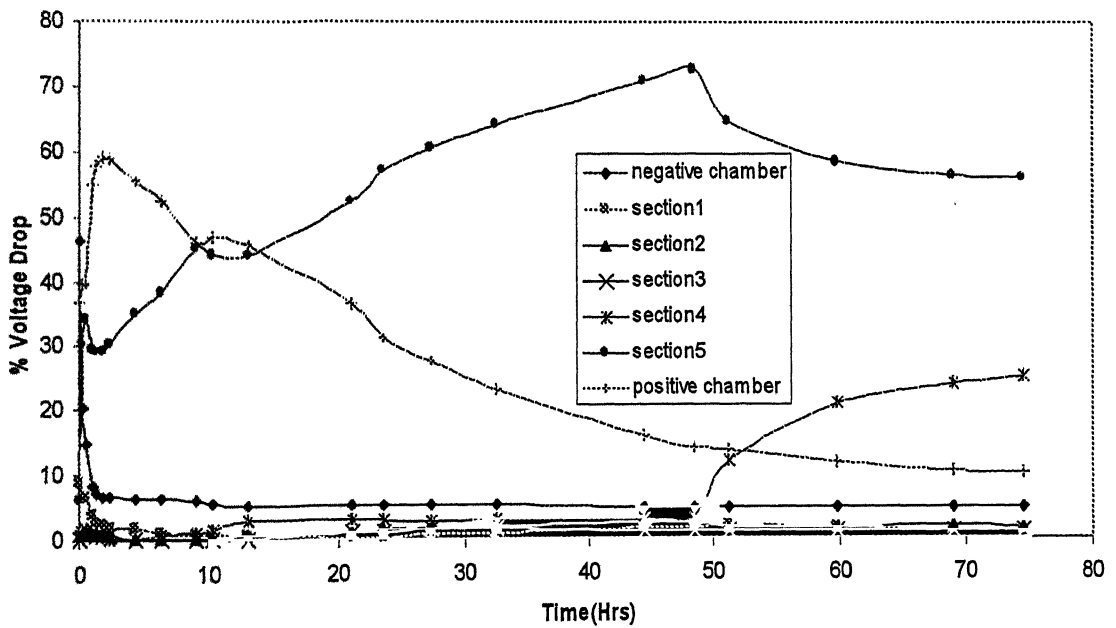


Fig 4.23 Percentage voltage drop at different sections of the tube for Kanpur soil for 25-volts

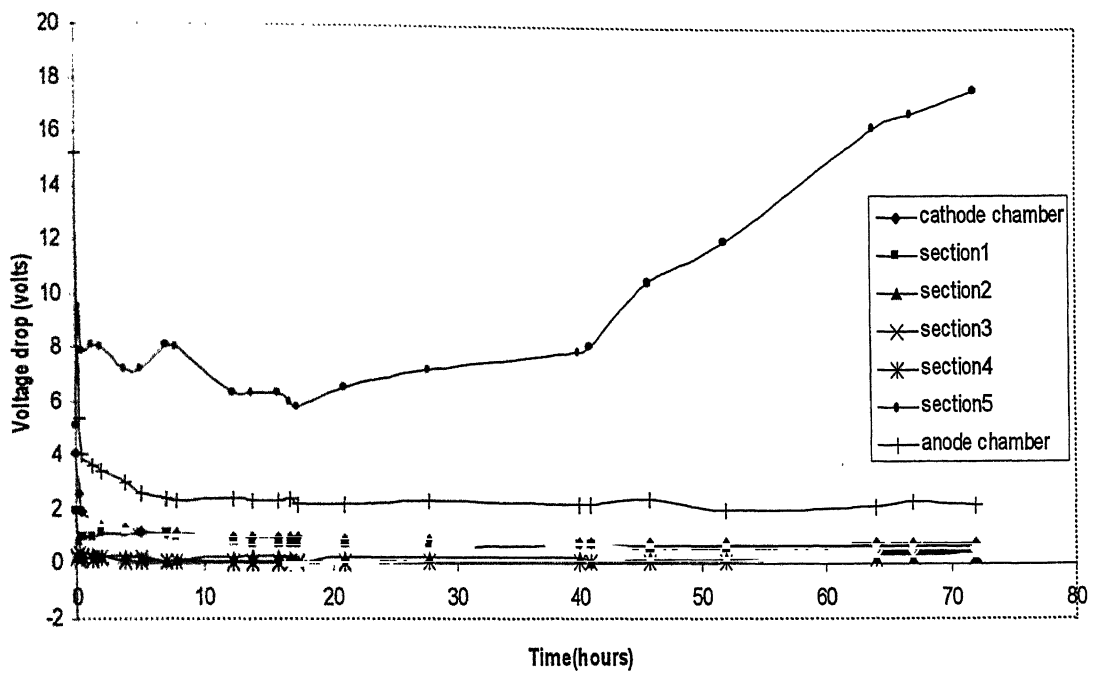


Fig 4.24 Voltage drop at different sections of the tube for Kanpur soil for 5mA

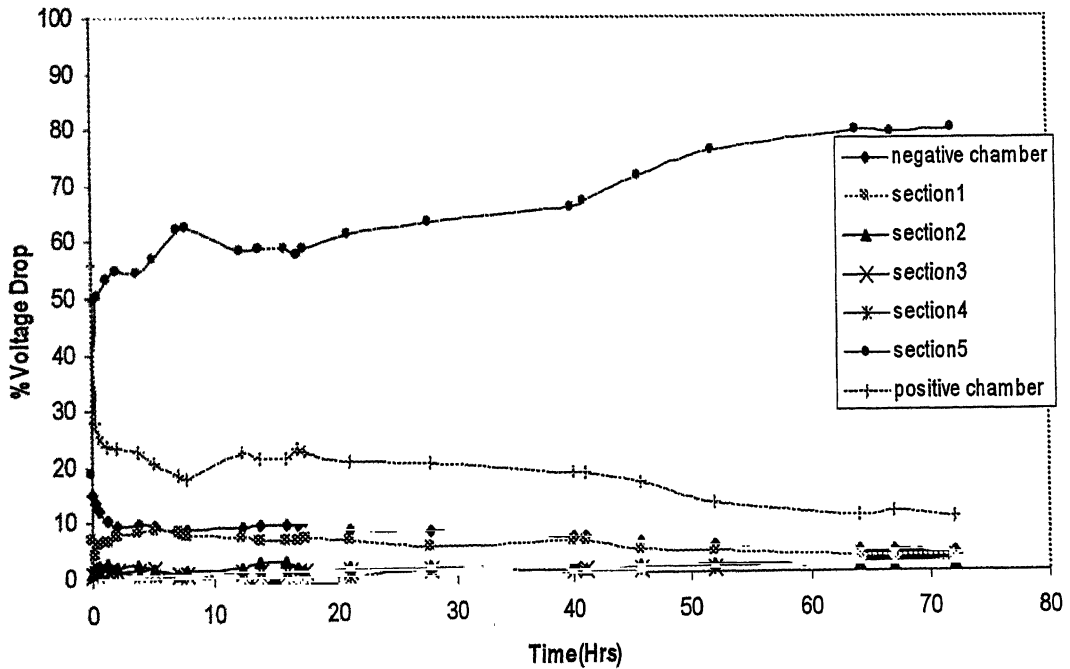


Fig 4.25 Percentage voltage drop at different sections of the tube for Kanpur soil for 5mA

Table 4.6 Voltage drop comparison between 5mA and 25-volts

	Time	cathode chamber	section1	section2	section3	seccion4	section5	anode chamber
5mA	6.25	1.6	0.3	0.1	0.1	0.2	9.6	13.1
25volts	5	1.2	1.1	0.2	0.2	0.1	7.2	2.6
5mA	10.25	1.4	0.2	0.1	0.1	0.4	11.1	11.7
25volts	12.25	1	0.8	0.2	0.1	0	6.3	2.4
5mA	21	1.3	0.1	0.3	0.3	0.8	13.1	9.1
25volts	21	0.9	0.7	0.2	0.1	0	6.5	2.2
5mA	32.5	1.3	0.2	0.5	0.4	0.8	16	5.8
25volts	27.75	0.9	0.6	0.2	0.1	0.1	7.2	2.3
5mA	51.25	1.2	0.5	0.4	0.3	3	16.2	3.4
25volts	52	0.8	0.6	0.2	0.1	0.1	12	2
5mA	74.5	1.2	0.3	0.4	0.3	6.3	14	2.5
25volts	72	0.8	0.6	0.2	0.3	0.4	17.7	2.2

4.3.2.2 Comparison between 10mA and 35-volts experiment for Kanpur soil

From Fig 4.27 the percentage Cr removed after 72 hours from Kanpur soil for 35-volts experiment is 78 percentages and in case of 10mA experiment it is 66 percentages. The maximum percentage of Cr is removed in the first 30 hours from the soil in case of 35-volts experiment and after that the rate falls. But the rate of removal of Cr in case of 10mA experiment is almost constant. The higher percentage of removal in case of 35-volts after 72 hours can be explained from Fig 4.30, which shows the percentage voltage drop at different sections in the tube for 35-volts experiment. From this figure it is clear that in section 5 the voltage drop is maximum. This section acts as an electroosmotic pump to draw the fluid to cathode chamber. From Fig 4.33 it can be clearly seen the difference in electroosmotic flow rate between potentiostatic and galvanostatic experiment. The rate in case of potentiostatic is much higher due to high voltage drop.

From Fig 4.29 and Table 4.7 the voltage drop across the tube initially in case of 10mA experiment is low, so the electroosmotic flux is also low. That's why the rate of removal for 10mA experiment is low initially and as the voltage drop across the tube increases (from Fig 4.31) with time the removal rate also increases, and speedy removal starts after 40hours.

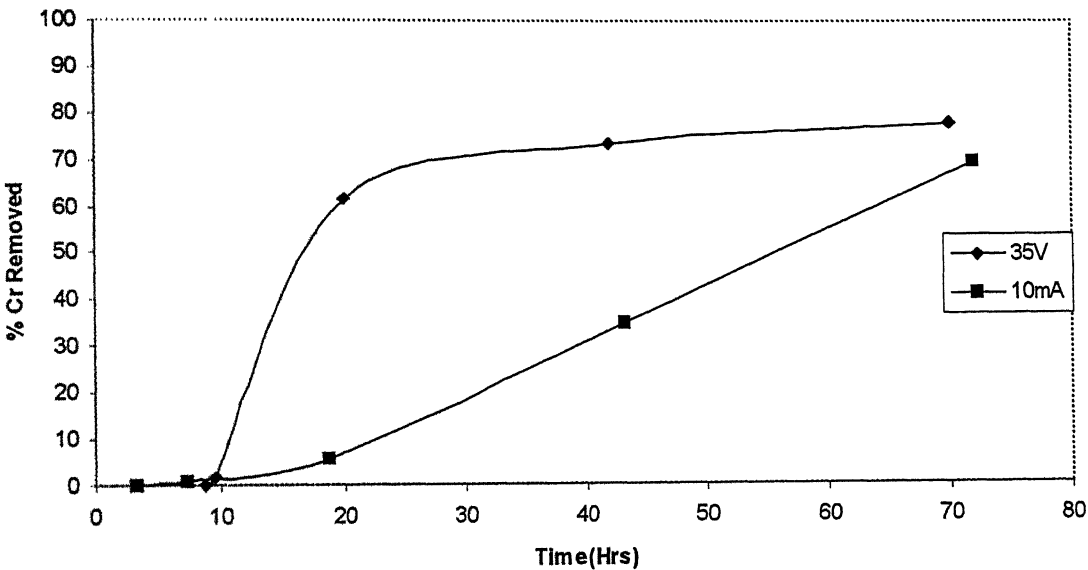


Fig 4.26 Percentage of Cr removed comparison between 10mA and 35-volts experiments (Kanpur Soil)

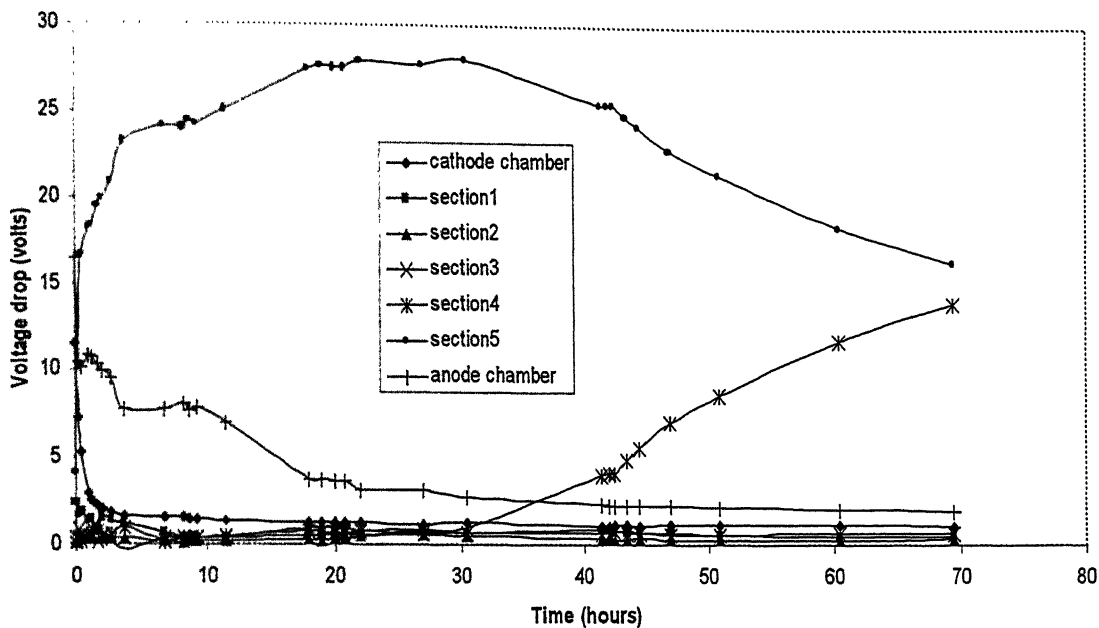


Fig 4.27 Voltage drop at different sections of the tube for Kanpur soil for 35-volts

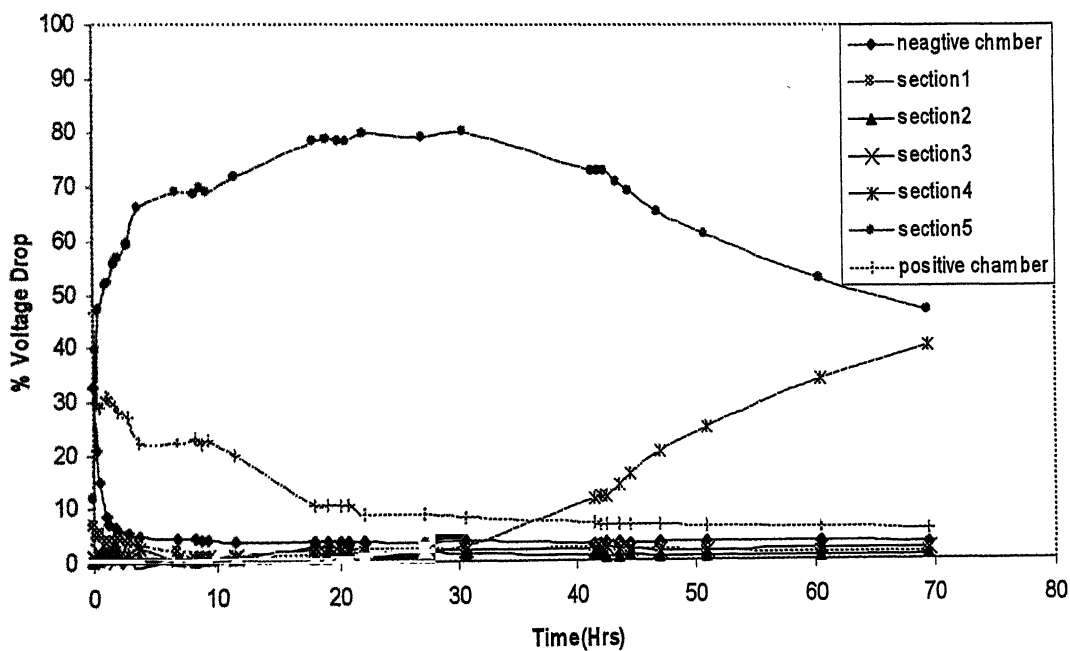


Fig 4.28 Percentage voltage drop at different sections of the tube for Kanpur soil for 35-volts

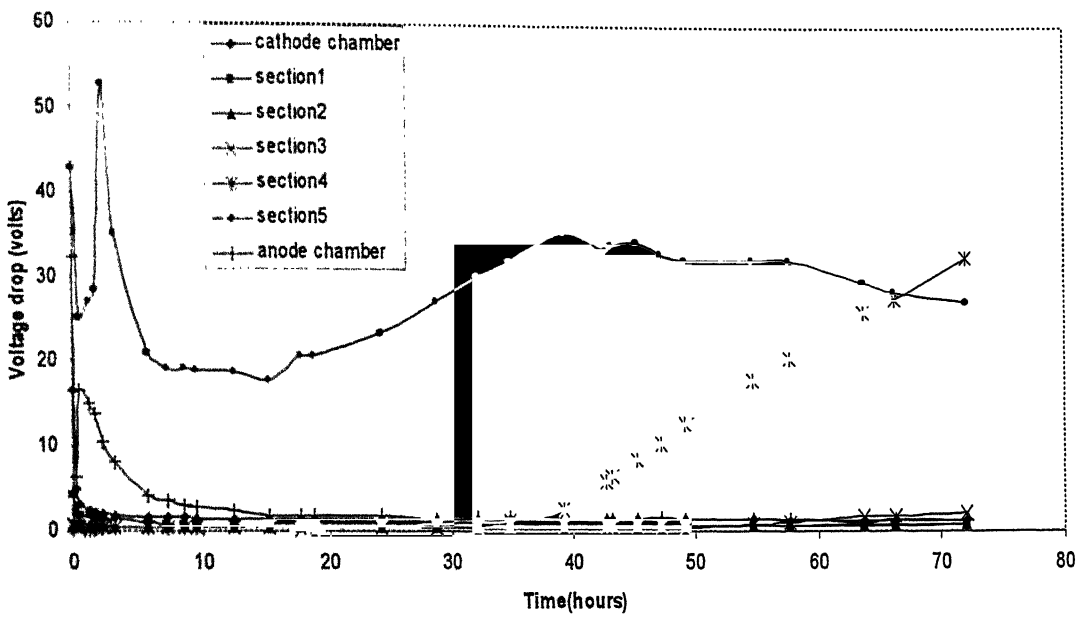


Fig 4.29 Voltage drop at different sections of the tube for Kanpur soil for 10mA

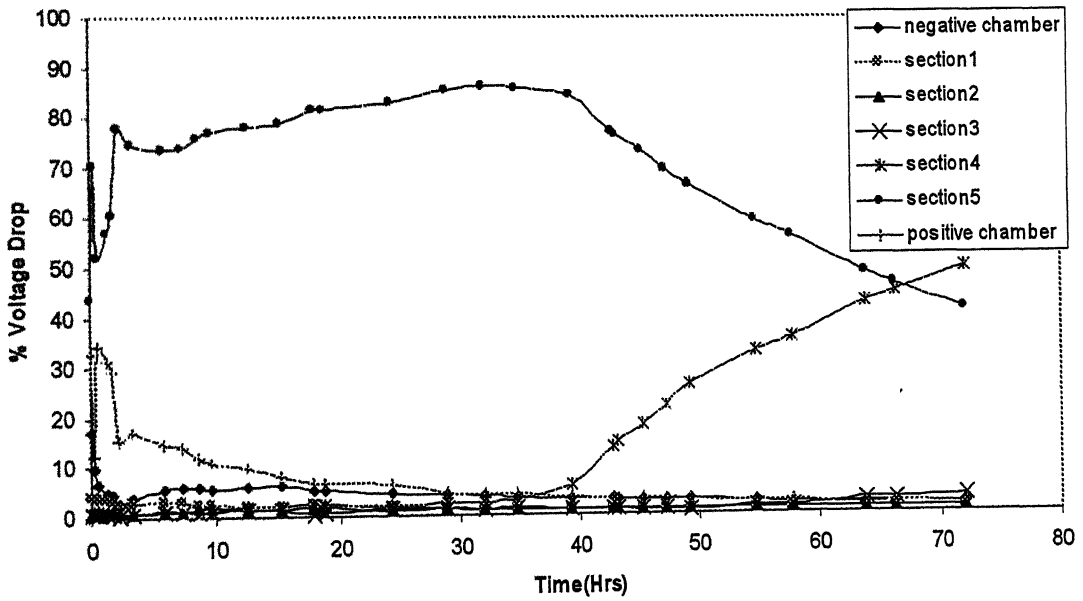


Fig 4.30 Percentage voltage drop at different sections of the tube for Kanpur soil for 10mA

Table 4.7 Voltage drop comparison between 10mA and 35-volts

	Time	cathode chamber	section1	section2	section3	section4	section5	anode chamber
10mA	5.75	1.6	0.9	0.3	0.3	0.4	21.1	4.2
35volts	6.75	1.6	0.7	0.2	0.4	0.2	24.1	7.8
10mA	9.5	1.4	0.6	0.4	0.3	0.3	18.9	2.7
35volts	9.25	1.5	0.4	0.2	0.4	0.4	24.2	7.9
10mA	18.75	1.3	0.5	0.4	0.2	0.6	20.7	1.7
35volts	19	1.3	0.5	0.2	1	0.7	27.6	3.7
10mA	32	1.3	0.4	0.4	0.4	0.9	30.1	1.5
35volts	30.5	1.3	0.7	0.5	0.7	1	28	2.8
10mA	49.25	1.3	0.4	0.5	0.4	12.7	32.1	1.3
35volts	51	1.2	0.6	0.3	0.6	8.7	21.4	2.2
10mA	72	1.2	0.7	0.7	2.2	32.5	27.1	1.2
35volts	69.5	1.1	0.5	0.4	0.7	14	16.3	2

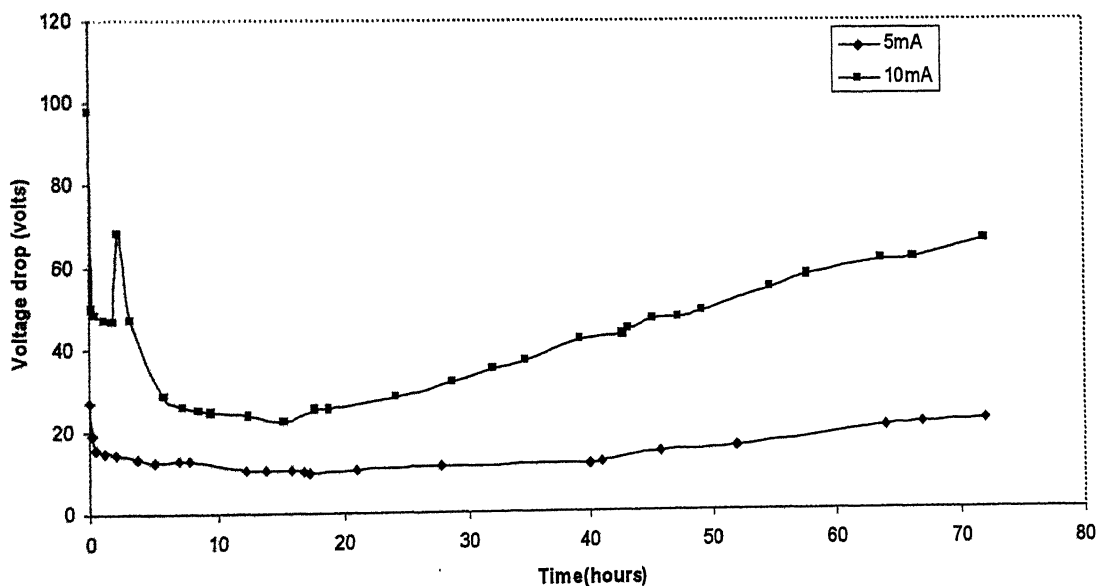
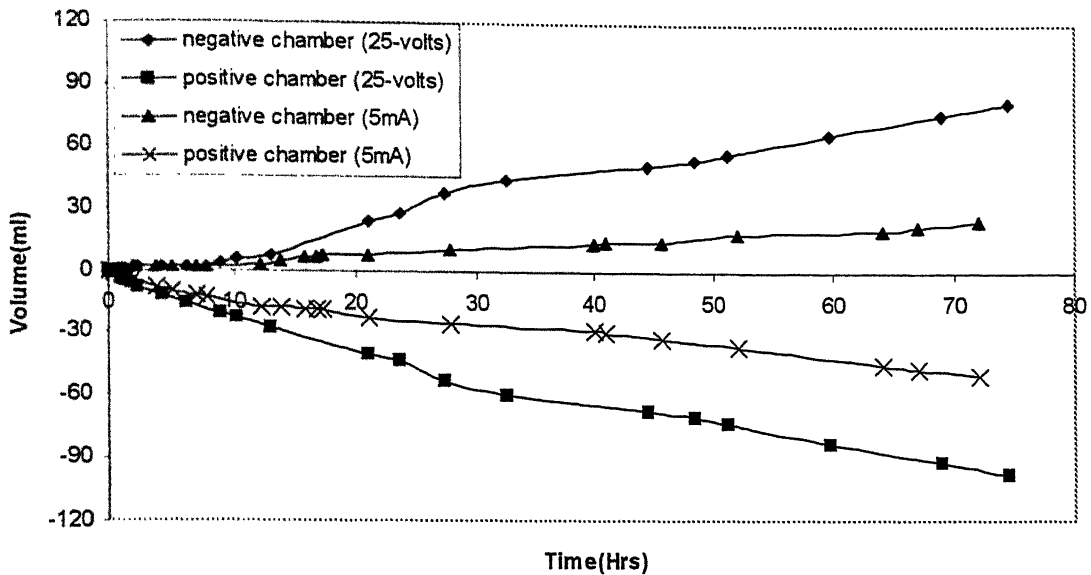
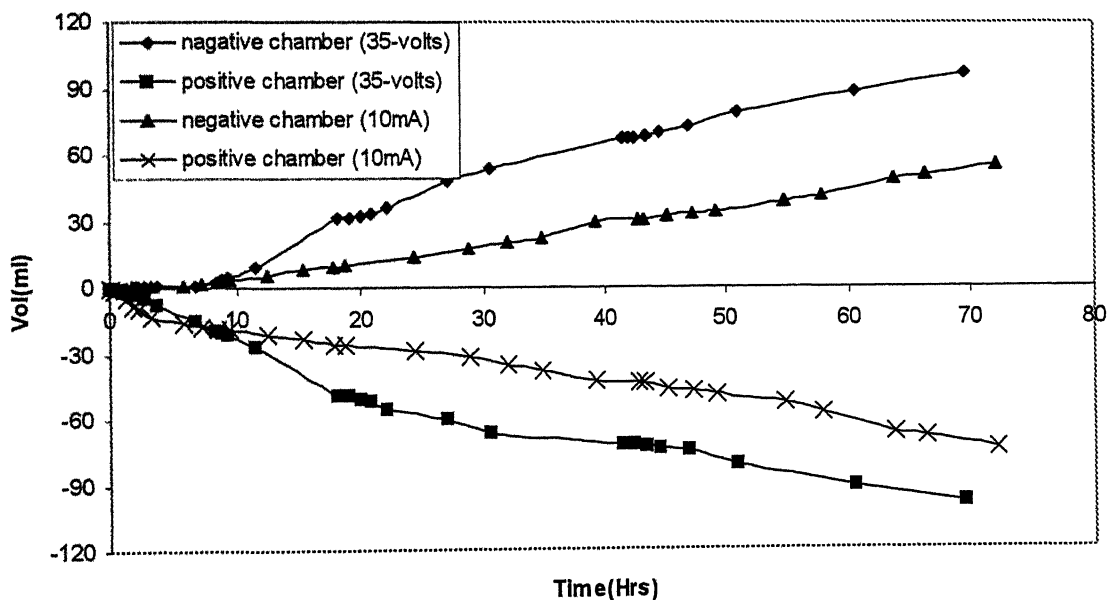


Fig 4.31 Total voltage drop across the tube for Kanpur soil , 5 and 10mA experiments



4.32 Comparison of electroosmotic flow between 25-volts and 5mA experiments for Kanpur soil



4.33 Comparison of electroosmotic flow between 35-volts and 10mA experiments for Kanpur soil

4.3.3 Specific Energy Consumption

The question that has to be addressed now is: Which of the two modes of operation, galvanostatic or potentiostatic, is more energy efficient? Energy efficiency will be determined in terms of specific energy consumption, which is defined as:

$$\text{Specific energy consumption} = \frac{\text{Total Energy consumed (watt - hour)}}{\text{Percentage of chromium removed}}$$

In case of kaolin experiments were carried out with different potentiostatic and galvanostatic conditions. From Fig 4.34 it is clear that the energy requirement per percentage of Cr removed for potentiostatic experiments is low, but the total percentage of chromium removed from kaolin is very low. In case of galvanostatic experiments, for 10mA the energy consumption is low but in case of 15mA experiment the energy requirement is high. But for both the cases the total percentage of Cr removed from kaolin is low. In case of 25mA experiment the total percentage of Cr removed is around 90 percentages and also the energy consumed per percentage of Cr removed is low as compared to 15mA experiment.

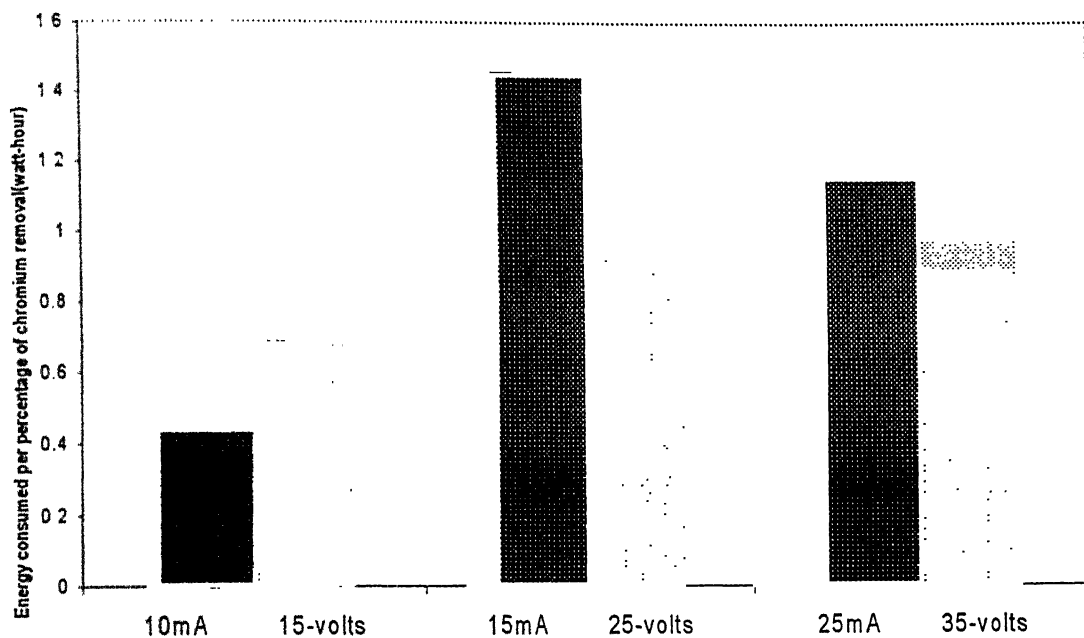


Fig 4.34. Energy consumed per percentage of chromium removed from kaolin for different potentiostatic and galvanostatic experiments.

In case of Kanpur soil, experiments were carried out with different currents and at different voltages. From Fig 4.35 the energy requirement per percentage of Cr removed can be seen. In case of constant voltage experiments the energy requirement per percentage of Cr removed is low, and also total percentage removal from soil is high. In case of constant current experiments for 5mA the energy consumption is low but the percentage removal is very low. If the energy consumption per percentage of Cr removed is compared with 25-volts experiment then it can be seen that the energy requirement in case of 5mA is higher than that of 25-volts. So the best case for remediation from Kanpur soil is to operate it with constant voltage to get higher efficiency of removal. It has been observed that in actual case the chromium gets removed in first 40 hours for the constant voltage experiment. So if we calculate the energy required for the percentage removal of chromium in 40 hours then energy efficiency will be much higher.

Similarly for 35-volts and 10mA experiment if the energy consumption is compared, there is higher energy consumption per percentage of Cr removed in case of 10mA than 35-volts.

From this we can conclude that for Kanpur soil the best operating parameter is to use constant current for the removal of Cr as the energy efficiency is much higher in this case than the constant current experiments.

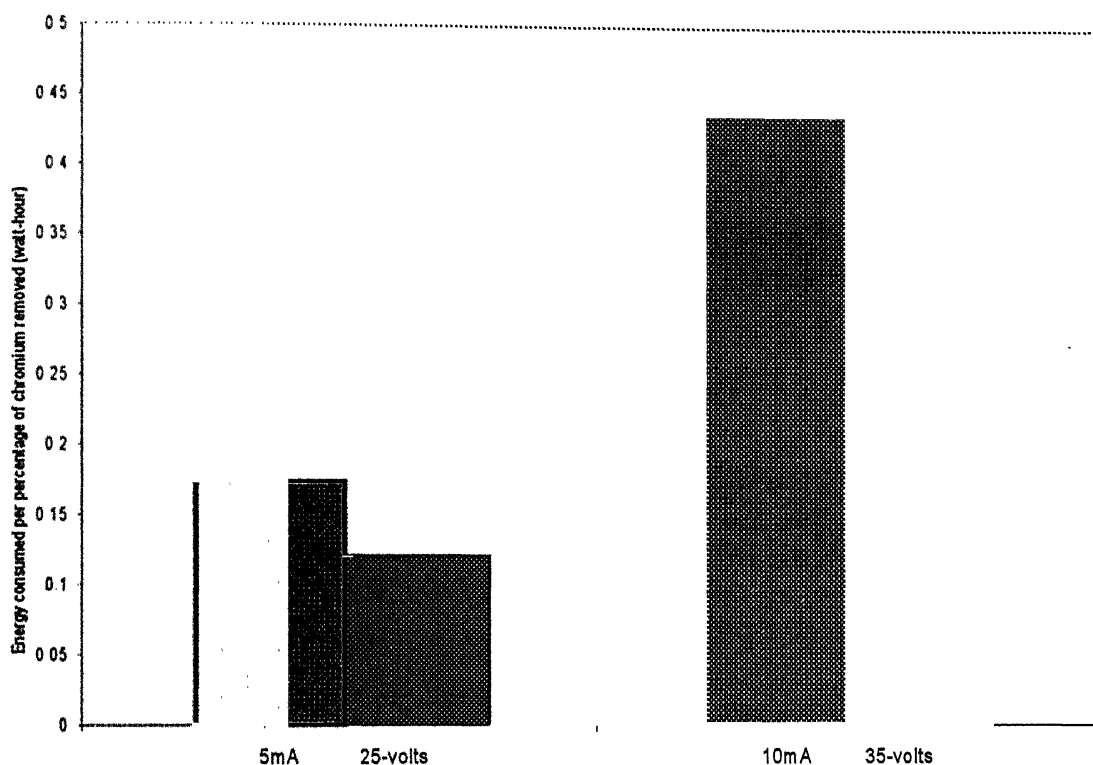


Fig 4.35 Energy consumed per percentage of Cr removed from Kanpur soil for different galvanostatic and potentiostatic experiments.

1. Kanpur soil and kaolin are cleaned predominately by electroosmotic and electromigration force respectively.
2. In case of Kanpur soil, higher percentage removed in potentiostatic mode but in case of kaolin, galvanostatic mode helps in removing high percentages.
3. Initial soil pH has a great role to play in deciding the operating mode: galvanostatic in acidic soil and potentiostatic in basic soil.
4. Operating in galvanostatic mode in case of kaolin and potentiostatic mode in case of Kanpur soil is energy efficient.
5. This also concludes that the best operating condition is to operate first 30 hours with constant voltage mode and rest with constant current mode in case of kaolin for energy efficient and high percentage removal.

The following features can be added in future:

1. Operating the experiment with potentiostatic mode for 30 hours and rest time with galvanostatic mode in case of kaolin.
2. Determination of scale-up criteria for the electrode placement.
3. Studies of 2-dimensional and 3-dimensional experiments with both mode of operation: Potentiostatic and Galvanostatic.
4. Development of mathematical models for optimization of process parameters.

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